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Characterization of Polydihydrosilane by SEC-MALLS and Viscometry

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Abstract

Silicon hydride compounds consisting of silicon and hydrogen constitute a fascinating class of silicon-based polymers because of their ability to form high-quality silicon film by solution-based process. In this study, we synthesize polydihydrosilane by photo-induced ring-opening polymerization of cyclopentasilane, and determine the molar mass, radius of gyration, and intrinsic viscosity of it in cyclohexene by size-exclusion chromatography combined with multi-angle laser light scattering and viscometry. It was found that the molar mass of polydihydrosilane ranges broadly from 10^2 to 10^6 g/mol. Both the intrinsic viscosity and radius of gyration exhibited a scaling behavior with respect to the molar mass with the intrinsic viscosity exponent $\alpha = 0.206$ and radius of gyration exponent $\nu = 0.410$. Classification of the polymer structure based on the α value suggests that the polydihydrosilane forms a branched-chain structure with a particle-like compact shape rather than a straight chain.

Keywords: cyclopentasilane, polydihydrosilane, SEC-MALLS

1. Introduction

Solution processes have attracted attention as methods for fabricating electronic devices because of their wide applicability and cost-effectiveness. We have previously demonstrated a fabrication of poly-silicon thin-film transistors using solution-processed amorphous silicon films obtained by pyrolysis of precursor solution consisting of polydihydrosilane $(\text{-(SiH}_2\text{)}_n\text{-)}$, cyclopentasilane (CPS: Si_5H_{10}), and organic solvent [1]. Subsequent to this study [1], pyrolysis experiments of soluble polysilane with the purpose to fabricate efficient emitters in the UV to IR spectral range for light emitting diodes have been reported recently Ref [2]. Both studies demonstrated solution-processed silicon devices. In particular, it indicates the possibility that polydihydrosilane solution has potential for applying to broad range of industrial applications such as large-area displays, solar cells, and photonic devices. For fabricating solution-processed silicon devices using polydihydrosilane, basic properties of the solution such as surface tension and wettability should be examined. From this perspective, we have reported that the surface energy of CPS and wettability of polydihydrosilane are dominated by van der Waals energy [3,4]. However, to date, systematic studies of the molar mass, molar mass distribution, and structure of the polydihydrosilane have not been investigated despite of the fact that they are essential to characterize the above properties.

In this paper, we synthesize polydihydrosilane by photo-induced ring-opening polymerization of CPS and characterize the molar mass distribution and structure of it by size-exclusion chromatography (SEC) combined with multi-angle laser light scattering (MALLS) and viscometry (SEC-MALLS-VISCOMETRY). It is empirically known that the polymer structure can be classified by viscosity exponent α and by radius of gyration exponent ν [5]. We also characterize the polymer structure by ^1H NMR and FT-IR. There have been some studies with regard to silicon-based polymers with alkyl side chains, in which SEC with light scattering and viscometry were applied [6–8]. However, there are no reports on the structure of polydihydrosilane that include a systematic study of the molecular distribution, except for a brief discussion of a GPC measurement related to photo-induced polymerization in our previous study [1].

2. Experiment

2.1 Sample preparation

Polydihydrosilane was synthesized by a photo-induced ring-opening polymerization of CPS to prepare carbon- and oxygen-free silicon films [1]. The synthesis and characterization of CPS are described in Appendix A. With the aim of probing the development of photo-induced polymerization, the polymers were synthesized under different conditions by changing the

irradiation time of UV light with constant wavelength and intensity. We selected UV light with the wavelength of 365 nm and intensity of 1 mW/cm². The irradiation times were 0, 15, 30, 45, 60, 90, 120, 180, and 240 min. The samples were prepared in a glove box filled with nitrogen gas (Scheme 1) because CPS and polydihydrosilane readily ignite in air.

It is important to choose suitable solvents for the SEC-MALLS-VISCOMETRY measurement. Toluene or decalin have previously been used as solvents for polydihydrosilane solution because the wettability, boiling point, and viscosity of these solvents are suitable for coating in solution processes. However, these solvent are not suitable for the present SEC experiment because of their poor solubility. We selected cyclohexene as a solvent. In order to avoid overloading of the column for the samples with higher irradiation times (higher molar mass), we examined the spectral change in chromatogram by varying the weight concentration of polydihydrosilane from 1.0×10^{-3} to 5.0×10^{-3} g/mL. The results showed no change for the positions of the peaks on the chromatogram in the above range of weight concentration. Thus, the weight concentration of 3.0×10^{-3} g/mL was selected.

As UV light source for the polymerization, Asahi Spectra LAX-101 with a xenon lamp was employed, and Ushio Accumulated UV Meter was used to calibrate the intensity of the light source. The oxygen level and dew point in the glove box were less than 0.5 ppm and -75 °C, respectively.

2.2 SEC-MALLS and viscosity measurements

The SEC-MALLS, viscometer, and refractive index (RI) detector were connected in series by stainless steel tubes, as shown schematically in Scheme 1. An injector was set in the glove box. The injected volume, flow rate, and temperature were 150 μ L, 1 mL/min, and 25 °C, respectively. Samples were inactivated by KOH solution after recording the measurements. Readings of the excess Rayleigh ratio $R(\theta)$ at a scattering angle θ , specific viscosity η_{sp} , and RI response were acquired every 0.5 sec during elution. The light scattering detector (DAWN-HELLEOS; Wyatt Technology), the viscometer (ViscoStar; Wyatt Technology), and the RI detector (Optilab rEX; Wyatt Technology) were connected to the SEC (1200 series; Agilent). The Shodex KF-805 column was used with a guard column attached to it. Wyatt Technology Astra V software was used for processing the data. Eighteen light detectors and a laser source of 658 nm were installed in the light scattering detector.

Astra V analyzed the data for each elution volume according to the following principle. The intensity (I) obtained from the RI detector is proportional to the differential refractive index Δn ($\Delta n = n - n_0$) according to the equation $I = K_{RI}\Delta n$, where K_{RI} , n , and n_0 are the RI constant, the refractive index of the solution, and the refractive index of the solvent, respectively. Also, Δn is expanded to

$\Delta n = (dn/dc)c$ for low-weight concentration c , where (dn/dc) is the refractive index increment. The mass recovery rate in SEC is defined by $\Sigma c_i/c_{injection}$, in which $c_{injection}$ and Σc_i are the injection weight concentration and the output total mass density obtained by summing c_i at the i th elution volume, respectively. Thus, $\Sigma c_i = \Sigma I_i \cdot K_{RI}/(dn_i/dc_i)$ is estimated by total area of the RI chromatogram, if (dn_i/dc_i) is constant. We describe the estimation of dn/dc for polydihydrosilane and CPS in Appendix B.

$R(\theta)$ was measured by photodetectors for each elution volume. The values of molar mass (M) and root-mean-square radius (radius of gyration, R_g) were estimated by plotting $\ln(K_{op}c/R(\theta))$ against $\sin^2(\theta/2)$, the Guinier-Zimm plot, with $K_{op} = (4\pi^2 n^2/N_A \lambda^4)(dn/dc)^2$, λ and N_A being the wavelength of incident light in vacuum and Avogadro's number, respectively. In the Guinier-Zimm plot which was devised for use with scattering from particles polydisperse in size and shape in the dilute polymer solution [9], $-\ln M$ is estimated from the intercept at $\theta \rightarrow 0$, whereas R_g is evaluated from the slope $d(\ln(K_{op}c/R(\theta)))/d(\sin^2(\theta/2))$ at the zero angle.

The differential viscometer detects the specific viscosity $\eta_{sp} = (\eta - \eta_0)/\eta_0$, where η and η_0 are the viscosity of the solution and the solvent, respectively. The intrinsic viscosity $[\eta]$ was determined by calculating η_{sp}/c directly for each elution volume. For the analysis of the polymer structure, we adopted the sphere model, which is based on the viscosity theory of colloidal particles, to analyse the molar mass dependence of $[\eta]$ [10]. In this model, $[\eta]$ is described by Eq. (1).

$$[\eta] = \frac{5}{2} \frac{N_A}{M} \frac{4\pi}{3} R_\eta^3, \quad (1)$$

where R_η is the viscosimetric radius. Starting from Eq. (1), we describe the scaling behavior of $[\eta]$ versus the molar mass.

2.3 ¹H NMR and FT-IR measurements

The molecular structure of the polydihydrosilane was examined using ¹H NMR (400 MHz; Bruker) and FT-IR (ALPHA; Bruker Optics). For the NMR measurement, the polydihydrosilane was dissolved in deuterated toluene (toluene-*d*₈), and tetramethylsilane (TMS: C₄H₁₂Si) was added as a reference. A tiny amount of CPS was added to the toluene-*d*₈ to enhance the solubility of polydihydrosilane. The FT-IR equipment was installed in the glove box.

3. Results and Discussion

3.1 Molar mass distribution

Fig. 1(a) shows the RI intensity for the four samples synthesized with irradiation times of 0, 30, 60, and 240 min (note that the data for samples with 15, 45, 90, 120, and 180 min are not shown). The sample displaying no irradiation (0 min) corresponds to CPS, and the inverted peak at the elution volume of 13 mL marks the end of sample. The RI chromatogram for CPS exhibits a sharp peak at the elution volume of 12 mL. The spectrum for the sample with a 30-min irradiation exhibits a broad peak at the lower elution volume in addition to the CPS peak with weak intensity. For the sample with a 60-min irradiation, the broad peak at the lower elution volume grows significantly, whereas the CPS peak disappears. This suggests the completion of photopolymerization of CPS to polydihydrosilane within 60 min of irradiation time.

The differential molecular weight fractions of polydihydrosilane are plotted as a function of the molar mass for the four samples in Fig. 1(b). The molar mass for polydihydrosilane ranges broadly from 10^2 to 10^6 g/mol. The molar mass distribution changes significantly for samples with the irradiation time of less than 60 min, whereas minor changes in molar mass distribution is observed for samples with irradiation times longer than 60 min. The sample with an irradiation time of 0 min has a sharp peak at the molar mass of 150 g/mol, confirming the existence of CPS. Hence, the decreasing intensity of the peak at 150 g/mol indicates how the molecular weight distribution spreads out when CPS is converted into polydihydrosilane during the first 60 min of irradiation. It suggests that polymerization induced by UV light developed rapidly. In the samples with an irradiation time of more than 60 min, the differential weight fraction in the high molecular weight region (10^5 – 10^6 g/mol) grows, which suggests a dispersive molecular distribution consisting of two components in these samples.

3.2 Elution profile of M , R_g , and $[\eta]$

Here, we discuss the details of the SEC-MALLS and viscosity measurements. In the MALLS detector, the data from three detectors placed on the side of the lower angle were excluded as they were likely to be noisy owing to stray light. Therefore, the data from 15 detectors setting at $\theta = 28$ – 141° were acquired. Fig. 2(a) shows the elution profiles of c , $R(90)$ at $\theta = 90^\circ$, and η_{sp} for polydihydrosilane with a 240-min irradiation. M and R_g in Fig. 2(b) and R_η and $[\eta]$ in Fig. 2(c) are estimated by method described in section 2.2.

With regard to the SEC measurement, it is first necessary to confirm the absence of a delay in elution. A comparison of the injected mass with the output mass obtained from the total area of the concentration chromatogram in Fig. 2(a) shows a mass recovery rate of 0.994, suggesting no absorption in the SEC column. This indicates that molecular size separation by SEC was successfully performed, and no elution delay was observed in the SEC column [11,12].

Since the R_g determined by SEC-MALLS has a minimum measurable size of > 10 nm, we employ the R_g data in region “A” ($R_g > 10$ nm) of Fig. 2(b), even though R_g shows a value less than 10 nm in the high elution volume side. The Guinier-Zimm plots at the upper and lower boundary of region “A” are shown in Figs. 3(a) and (b), respectively.

The antilogarithm of the intercept to the vertical axis and the slope of the regression line at $\theta \rightarrow 0$ in Fig. 3(b) yielded $M = (4.457 \pm 0.245) \times 10^6$ g/mol and $R_g = (18.6 \pm 0.0)$ nm, whereas those in Fig. 3(a) provided $M = (1.099 \pm 0.003) \times 10^6$ g/mol and $R_g = (10.0 \pm 0.1)$ nm. This indicates that R_g at the elution volumes of 7.5 and 8.2 mL contain the relative errors of $\sim 0\%$ and 1.0%, respectively, whereas M at the same volumes exhibit errors of 5.5% and 0.3%, respectively. It is well known that unsuitable preparation of the sample as well as low sensitivity of the detector lead to a low linearity of the Guinier-Zimm plot, resulting in an increase in error. In our sample, $n_{\text{polymer}} = 1.7678$ at 589 nm [3], $n_0 = 1.4466$, and $dn/dc = 0.2727$; therefore, high sensitivity for RI and MALLS detection is expected. As a result, an excellent linearity of the Guinier-Zimm plot is obtained, as shown in Fig. 3. However, considering the detection limit of R_g , we adopted the R_g values in region “A” for the R_g - M plot assuming the relative error of 5.4% for M .

3.3 Structure of the polymer

Here, we explore the structure of polydihydrosilane on the basis of the scaling behavior of $[\eta]$ and R_g . Logarithmic plots of $[\eta]$ versus M and R_g versus M for the sample with the irradiation time of 240 min are shown in Figs. 4(a) and (b), respectively. These plots exhibit a scaling feature, which is fitted by linear function described in Eq. (2a) (for $[\eta]$) or Eq. (2b) (for R_g):

$$[\eta] = 0.414M^{0.206}, \quad (2a)$$

$$R_g = 0.033M^{0.410}. \quad (2b)$$

The scaling relation $[\eta] = KM^\alpha$ is known as the Mark-Houwink-Sakurada equation [5]. The data fitted by Eq. (2a) accord well with the scaling relation. The solid line in Fig. 4(a) was fitted to $[\eta]$ between 10^3 and 3×10^6 g/mol, whereas the solid line in Fig. 4(b) was obtained by fitting R_g between 1.099×10^6 and 4.457×10^6 g/mol in region “A” of Fig. 2(b).

Here we focus on the fitting of $[\eta]$ versus M and interpret the scaling behavior on the basis of the sphere model [10]. Since $[\text{SiH}_2]$ (mass $M_m = 30.102$ g/mol) is considered to be a monomer unit of polydihydrosilane, the degree of polymerization (number of monomer units: N) for a polymer with molar mass M is given by $N = M/M_m$. Thus, the radius of gyration may be written as

$$R_g = aN^\nu, \quad (3)$$

where a denotes the “effective length” of $[\text{SiH}_2]$. By substituting Eq. (3) into Eq. (1) and by using the parameter $\rho = R_\eta/R_g$, the Mark–Houwink–Sakurada equation of $[\eta] = KM^\alpha$ is obtained, where $\alpha = 3\nu - 1$ and the coefficient K is given by

$$K = \frac{10\pi}{3} \left(\frac{\rho a}{M_m^\nu} \right)^3 N_A. \quad (4)$$

According to the present sphere model, the radius of gyration exponent is estimated to be $\nu = 0.402$ for $\alpha = 0.206$. Since $\nu = 0.410$ in Eq. (2b), the agreement between the two results suggests that the sphere model for the viscosity can be appropriately applied to polydihydrosilane with monomer unit $[\text{SiH}_2]$.

As described in Appendix C, this polydihydrosilane/cyclohexene system at 25 °C has a positive value of A_2 , which corresponds to a good solvent condition. Therefore, if the polydihydrosilane has a straight-chain structure, α should be in the range from 0.5 for Flory theta solvent to about 0.8 in a good solvent [5]. However, the experimental value of 0.206 was much smaller than the cut-off value for a straight-chain polymer. Thus, we can presume that the polydihydrosilane exists as a branched-chain structure.

With respect to the polymer shape, $\rho = R_\eta/R_g$ gives a measure of the compactness of the molecular geometry by comparing its hydrodynamic dimensions. It was pointed out for polystyrene that the values $\rho = 0.76$ and $\rho = 1.29$ correspond to a straight chain polymer and a rigid sphere, respectively [13]. Using $R_\eta = (3[\eta]M/10\pi N_A)^{1/3}$ with Eqs. (2a) and (2b), $\rho = 1.222(M)^{-0.008}$; accordingly, $\rho = 1.09$ and $\rho = 1.08$ are determined for $M = 1.099 \times 10^6$ and 4.457×10^6 g/mol, respectively. This suggests that the polydihydrosilane has a particle-like compact shape. For $\rho = 1.09$ using Eq. (4) and $K = 0.414$ mL/g in Eq. (2a), a is estimated to be 0.145 nm. This value agrees well with the bond lengths between Si and H in various molecules [14,15].

To probe the branching of polydihydrosilane, we carried out the ^1H NMR and FT-IR measurements, and analyzed the data by assuming tri-functional branching points consisting of SiH groups. In the analysis, we focused on the number ratio of SiH_2 to SiH groups. Fig. 5 shows the ^1H NMR spectrum of polydihydrosilane with the irradiation time of 240 min. The peak at 3.25 ppm results from added CPS. The band-like signals at 3–4 ppm are due to intermolecular interactions among the polymers as well as intramolecular interactions. According to the assignments by Sudarshan et al. [16] and Gollner et al. [17], the sharp peaks and the band in the range of 4.0–3.2 ppm are attributed to the hydrogens of the SiH_2 and SiH_3 groups, whereas the peaks at the higher magnetic field range of 3.2–2.9 ppm are associated with the hydrogen of the SiH group. In Fig. 5,

the area for the signals in the range of 4.0–3.2 ppm was 11.91 when the area for those in the range of 3.2–2.9 ppm was set to 1. Since one branching point (SiH) gives one terminal group (SiH₃), the numbers of SiH and SiH₃ groups are almost the same for branched polymers. Thus, the area of 8.91 should be associated with the hydrogens of SiH₂ groups; accordingly, the number ratio of SiH₂ to SiH groups is evaluated to be 4.5.

Next we analyze the FT-IR spectrum for polydihydrosilane according to the assignment of the molecular vibration of SiH and SiH₂ in hydrogenated amorphous silicon [18]. Fig. 6 shows our FT-IR spectrum for polydihydrosilane with a 240-min irradiation in the wavenumber (ω) range of 1850–2150 cm⁻¹. It is evident that the broad band at around 2100 cm⁻¹ is separated into two bands using the Gaussian function as indicated by dotted lines in Fig. 6. The spectral feature is very close to ones in Ref.[18] in which the absorption bands around 2100 and 2000 cm⁻¹ are attributed to the stretching mode of SiH₂ and SiH groups, respectively. In those references [18,19], the hydrogen content (N_{Hi}) with the mode i is evaluated by using Eq. (5).

$$N_{Hi} = A_i \int \frac{\alpha(\omega)}{\omega} d\omega, \quad (5)$$

where α is absorption coefficient and A_i is the proportionality constant. So the number ratio of SiH₂ to SiH groups, i.e., $N_{H2100}/2N_{H2000}$ may be evaluated by FT-IR spectrum of polydihydrosilane in Fig. 6, assuming $A_{2100} = 2.2 \times 10^{20}$ cm⁻² and $A_{2000} = 9.0 \times 10^{19}$ cm⁻² [19]. The number ratio of SiH₂ to SiH groups estimated from the dotted lines in Fig. 6 is 4.1.

The scaling exponents, ¹H NMR data, and FT-IR data give us a speculative picture of the features of polydihydrosilane indicating the structure of a branched polymer with a particle-like compact shape having a three-functional branch point in the form of SiH for every 4.1–4.5 units of SiH₂. Thus, the relationship between R_g and the branched structure is discussed by applying a subunit (blob) analysis [20]. Let us group the monomers of [SiH₂] in the blobs with size ξ , composed of g elements i.e. g being the average number of [SiH₂] between tri-functional units [SiH]. From a scaling consideration of the blobs, the R_g may be written with use of ξ as

$$R_g = (N/g)^\nu \xi. \quad (6)$$

Comparing Eq. (3) with Eq. (6), $\xi = ag^\nu$, so that $\xi = 0.269$ nm for $\nu = 0.410$, $g = 4.5$, and $a = 0.145$ nm. Since the effective size of CPS is estimated to be about 0.3 nm [21], these suggest the branching of polydihydrosilane is initiated mainly from the ring-opening reaction of CPS resulting

in a blob composed of four [SiH₂] monomers and one [SiH] and a hydrogen. However, more comprehensive details for the growth of the branching and its geometry, such as comb chain, randomly branched, or cross linked are not evaluated in this study.

4. Conclusions

The molar mass, molar mass distribution, and structure of polydihydrosilane synthesized by photo-polymerization from CPS have been explored using the SEC-MALLS-VISCOMETRY system. The measurements required the selection of a solvent, in which the polymer had good solubility, and an SEC-MALLS system connected to a sample-preparation box that could function in an inert atmosphere. Achieving these two requirements made the measurements possible.

It was found that the molar mass ranges broadly from 10² to 10⁶ g/mol in samples with 240-min irradiation at the wavelength of 365 nm and the intensity of 1 mW/cm². The $[\eta]$ and R_g values versus the molar mass agreed well with the scaling law, and as a result, the scaling exponents were determined ($\alpha = 0.206$ and $\nu = 0.410$) using the appropriate solvent. The sphere model based on the viscosity theory of colloidal particles gave a consistent description of the scaling of $[\eta]$ with R_g . It is concluded that polydihydrosilane has a branched structure with a particle-like compact shape in cyclohexene at 25 °C. The existence of a branch point (SiH) for every 4.1–4.5 units of SiH₂ was estimated with the help of ¹H NMR and FT-IR. The relationship between R_g and the branched structure suggests the blob structure in a manner consistent with ring-opening reaction of CPS. Although the general features of the polymer structures were elucidated, the details of geometric structure for polydihydrosilane have not yet been clarified. Therefore, further analysis of spectroscopic data from NMR, UV, and FT-IR based on the first-principle calculations of molecular structure and vibrational spectra [21] should be conducted. In general, the molar mass feature, viscosity, and structure of polydihydrosilane determined in this work provide valuable data for applications of this material to solution-processed devices such as thin film transistors and solar cells.

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Appendix A: Synthesis and characterization of CPS

The starting material (CPS) was synthesized according to the procedure of Hengge et al. [22–24] as follows. Diphenyldichlorosilane (56 mL, 260 mmol) was added dropwise to a stirred suspension of lithium (3.6 g, 520 mmol) in tetrahydrofuran (200 mL) over a period of 1 h, and the resulting mixture was stirred for 11 h. The reaction mixture was poured into cold water (300 mL). The precipitates were collected by filtration, washed with water, dried in vacuo, and recrystallized from a mixture of ethyl acetate and cyclohexane (1:1) to give a white powder (decaphenylcyclopentasilane, 32 g). A suspension of decaphenylcyclopentasilane (30 g, 33 mmol) and aluminum chloride (1 g, 7 mmol) in cyclohexane (100 mL) was stirred at room temperature for 6 h with continuous bubbling of dry hydrogen chloride gas to give decachlorocyclopentasilane. The remaining hydrogen chloride was removed by bubbling N₂ through the solution. The solution of decachlorocyclopentasilane in cyclohexane was added dropwise to a suspension of lithium aluminum hydride (10 g, 260 mmol) in diethyl ether (30 mL) at 0 °C, and the resulting mixture was stirred for 12 h. Then, the reaction mixture was filtered. The filtrate was concentrated, and the residue was distilled under reduced pressure to afford pure cyclopentasilane (17 g) as a colorless liquid (GC purity > 99%). The CPS was characterized by ¹H NMR (400 MHz; Bruker), ²⁹Si NMR (80 MHz; Bruker), FT-IR (ALPHA; Bruker Optics), and GC-MS (GC-17A + QP-5000; Shimadzu). ¹H NMR (toluene-*d*₈) δ = 3.25 ppm(s); ²⁹Si NMR (toluene-*d*₈) δ = -107.0 ppm; FT-IR (neat) ν = 2132(s), 897(s), 863(w), and 710(s) cm⁻¹; MS(EI) *m/z* = 149.95 (30%, Si₅H₁₀), 140.85 (19%), 139.85 (21%, Si₅), 119.90 (13%), 118.90 (22%), 117.90 (100%, Si₅H₁₀-SiH₄), 116.90 (26%), 115.90 (75%), 114.90 (19%), 113.90 (25%), 112.90 (44%), 111.85 (39%, Si₄), 85.90 (21%, Si₅H₁₀-2SiH₄), 84.95 (31%), 83.90 (24%, Si₃), 57.00 (10%), and 56.00 (8%).

Appendix B: Determination of *dn/dc*

The *dn/dc* is an essential parameter for analysis by SEC-MALLS. Here five solutions at different concentrations were prepared and their differential refractive indexes (Δn) were measured using the RI detector. The results for CPS and polydihydrosilane in cyclohexene at 25 °C are shown in Fig. B, where one set of data that led to the largest deviation from the regression line was excluded from the plot. The *dn/dc* values obtained for CPS and polydihydrosilane were 0.2133 ± 0.0024 and 0.2727 ± 0.0024 mL/g, respectively. In this study, the *dn/dc* value of 0.2727 mL/g was adopted as the average value of various molar mass distributions. For the sample with coexisting CPS and polydihydrosilane, we used *dn/dc* = 0.2133 mL/g for the CPS peak (elution volume = 11.6–12.2 mL), and used *dn/dc* = 0.2727 mL/g for the broad peak in the lower range of elution volume (less than 11.6 mL).

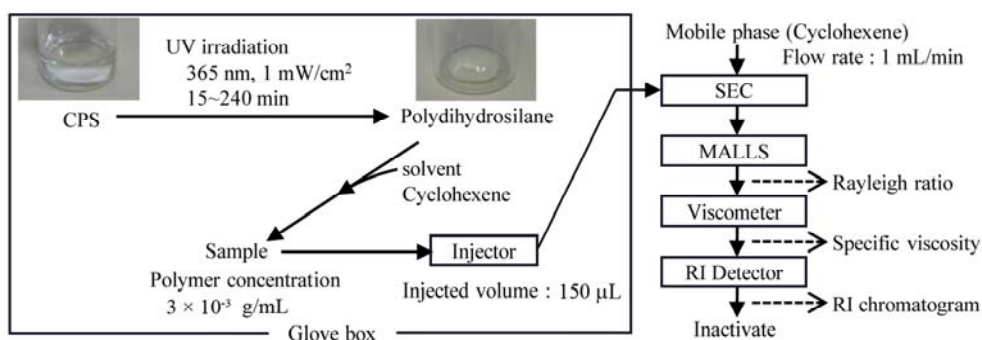
Appendix C: Batch measurement of MALLS

Since the scaling exponents α and ν depend on the solubility of the polymer in the solvent, the estimation of the second virial coefficient (A_2) is important for the discussion of the relationship between α (or ν) and the polymer structure. We measured A_2 of the polydihydrosilane/cyclohexene system at 25 °C by batch mode using MALLS with four solutions of different concentrations ranging from 6×10^{-4} to 3×10^{-3} g/mL. The result is shown in Fig. C using the Guinier-Zimm plot. The value of A_2 is determined to be $1.100 \pm 0.057 \times 10^{-3}$ mol·mL/g², indicating that cyclohexene is a good solvent for polydihydrosilane at 25 °C.

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Scheme 1 Schematics of sample preparation and the SEC-MALLS-VISCOMETRY system. Within a glove box under an inert atmosphere ($O_2 \leq 0.5$ ppm, dew point ≤ -75 °C), polydihydrosilane was synthesized by UV irradiation of CPS. The photographs indicate the change of the liquids from CPS to polydihydrosilane. The sample preparation and SEC-MALLS-VISCOMETRY measurements were carried out at 25 °C.

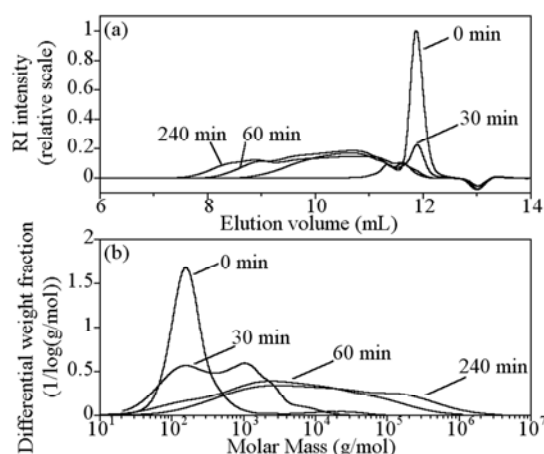


Fig. 1 SEC-MALLS result for CPS and polydihydrosilane synthesized with irradiation time 30, 60 and 240 min dissolved in cyclohexene at 25 °C. (a) RI intensity. (b) Molar mass distribution.

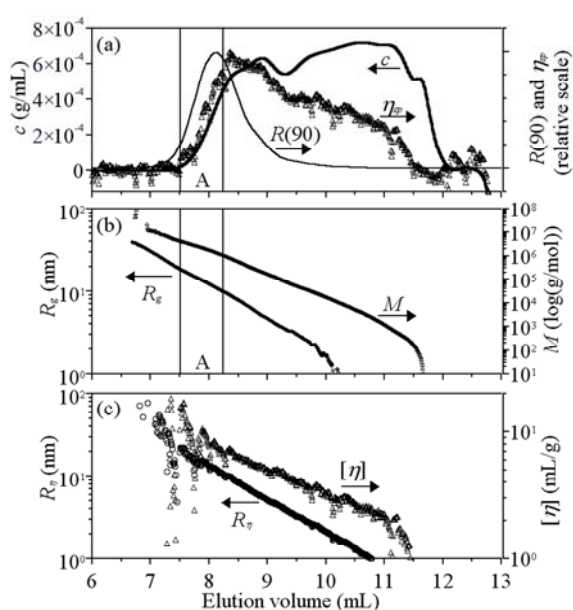


Fig. 2(a) Elution profile of c , $R(\theta = 90^\circ)$, and η_{sp} for polydihydrosilane with a 240-min irradiation dissolved in cyclohexene at 25 °C. (b) M and R_g vs. elution volume. (c) R_η and $[\eta]$ vs. elution volume. The region designated as “A” is adopted for the scaling analysis of the R_g – M plot, in which R_g is within the detection limit (>10 nm).

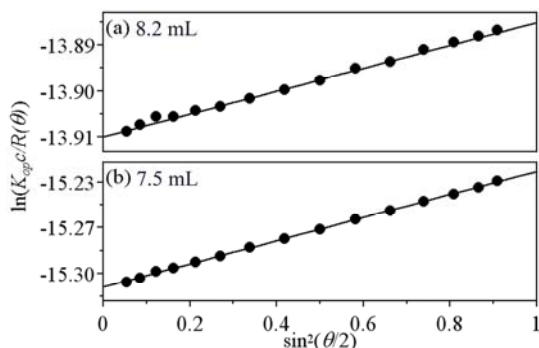


Fig. 3 The Guinier-Zimm plot “ $\ln(K_{op}c/R(\theta))$ vs. $\sin^2(\theta/2)$ ” at the elution volume of (a) 8.2 mL and (b) 7.5 mL. M and R_g for polydihydrosilane were obtained from these plots of each elution volume slice at 25 °C. Cyclohexene was used as the solvent.

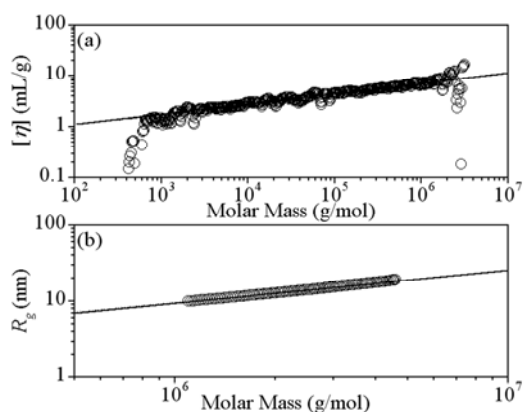


Fig. 4 Log–log plot of (a) $[\eta]$ vs. M , (b) R_g vs. M for polydihydrosilane with a 240-min irradiation dissolved in cyclohexene at 25 °C. The solid lines in Fig. 4(a) and (b) represent the linear fits of $[\eta]$ and R_g , respectively.

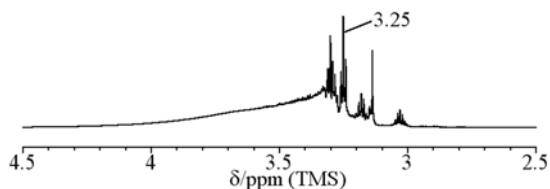


Fig. 5 ^1H NMR spectrum of polydihydrosilane with a 240-min irradiation in toluene- d_8 at 25 °C.

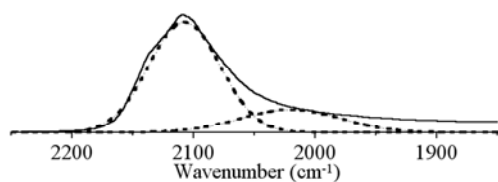


Fig. 6 FT-IR spectrum of polydihydrosilane with a 240-min irradiation at 25 °C.

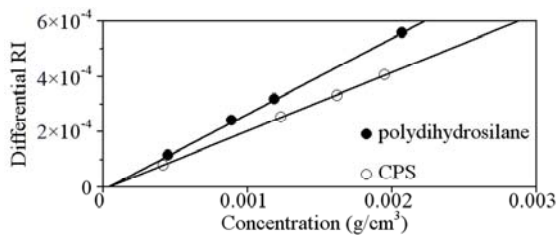


Fig. B Δn vs. c of CPS and polydihydrosilane in cyclohexene at 25 °C. Linear fitting of the data from both samples gives $dn/dc = 0.2133 \pm 0.0024$ mL/g (CPS) and $dn/dc = 0.2727 \pm 0.0024$ mL/g (polydihydrosilane).

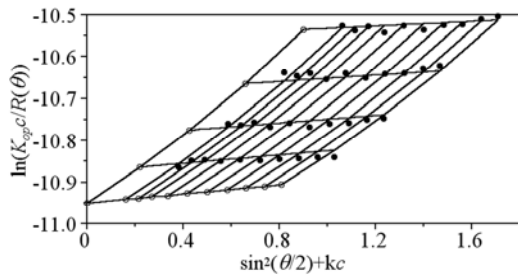


Fig. C Guinier-Zimm plot of batch mode light scattering from polydihydrosilane with a 240-min irradiation dissolved in cyclohexene at 25 °C. $M = 5.695 \pm 0.055 \times 10^4$ g/mol, $R_g = 7.0 \pm 6.7$ nm, and $A_2 = 1.100 \pm 0.057 \times 10^{-3}$ mol·mL/g².