Polymerization of Phenylacetylene-Based Monodendrons and Structure of the Corresponding Polydendrons

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ABSTRACT: Monodendrons consisting of *m*-linked phenyleneethynylene repeating unit with trimethylsilyl-, pentamethyldisiloxanyl-, and nonamethyltetrasiloxanyl- peripheral groups were synthesized using the convergent approach. The focal point of monodendrons, terminal acetylene, was polymerized with Rh catalyst to give the corresponding polydendrons with a high molecular weight, *e.g.*, $\overline{M}_w = 2.8 \times 10^6$ ($\overline{DP} = 2.8 \times 10^3$). The polydendrons showed good solubility in common organic solvents, and good membrane forming ability. Since we obserbed high ratio of a peak at δ 5.8–6.0, assignable to *cis* proton of poly(phenylacetylene) main-chain, in ^{1}H NMR of the polydendrons, the polydendrons were found to be *cis*-rich polymer. The visible absorption maxima (λ_{max}) of the polydendrons significantly increased due to effect of the bulky substituents at *m*-position in comparison with the corresponding zero generation of poly(phenylacetylene) derivatives having no substituents at *m*-position. The wide angle X-Ray scattering of the polymers suggested the pseudohexagonal lattice of rod-like molecules. The interplanar *d* spacing increased with increasing generation or size of the peripheral silyl group.
KEY WORDS Poly(phenylacetylene) / Molecular Architecture / Dendrimer / Polydendron / Cylindrical Macromolecule / Phenyleneethynylene / Conjugated Polymer /

Recently, dendrimers have attracted much attention in organic and polymer chemistry as the macromolecules with novel properties or functions depending on their specific shapes with precisely defined three-dimensional structures.[1] A great number of various dendrimers have been synthesized with the explosive growth of this area, and also the shapes of the dendrimers have not been only globular type. A new class of dendrimers with a core group of polymer backbone instead of a dot-like molecule are known as the side chain dendritic polymers or dendronized polymers,[2] and various core polymers have been reported in the last decade, *i.e.*, poly(ethyleneimine),[3] poly(styrene),[4−9] poly(vinyl ether),[10] poly(methacrylate),[5, 6, 8, 11, 12] poly(propellane),[13] poly(phenylene),[13, 14] poly(methacrylamide),[15] poly(phenylacetylene),[16] poly(oxanorbornene),[17] poly(phenylenevinylene),[18] poly(amide),[19, 20] poly(triacetylene),[21] poly(phenyleneethynylene),[22] poly(acrylate),[23] poly(imide),[20] poly(thiophene)[24] and poly(fluorene).[25] The cylindrical or worm-like structures for some of them were confirmed by X-Ray diffraction (XRD), scanning force microscopy (SFM), light scattering, viscosimetry and other experimental techniques.

The side chain dendritic polymers can be synthesized from the corresponding core polymers, using the same methodology as usual dendrimer syntheses, *i.e.*, the divergent and convergent approach. However, these methods are undesirable for making regularity of a repeating chain structure because it is difficult for polymer reactions such as these methods to complete attachment of the dendron-building blocks or the monodendron onto a reactive polymer chain. This difficulty of the polymer reactions is increased by the increasing steric hindrance of reactive sites with the generation and conversion of dendron.

An alternative synthetic approach has been focused on the polymerization of monodendron, which is preferred to the polymer reaction methods. But it was also difficult for homo-polymerization of monodendron monomers over the second generation to achieve a high degree of polymerization (DP) due to steric hindrance of the bulky side chain dendron, *e.g.*, most of the polymerized monodendrons (*i.e.*, polydendrons) resulted in DP < 100, although the degree of polymerization was improved by copolymerization with unbulky comonomer, or by polymerization of monomers connecting a dendron group with a polymerizable group by a spacer unit.[4a,6]

We previously reported that we succeeded in obtaining polydendrons with extraordinary high degrees of polymerization, whose dendron unit was constructed of phenylene ethynylene repeating units, and whose main chain was poly(phenylacetylene).[16] It is known that poly(phenylacetylene)s were yielded by some rhodium complex catalysts with high degrees of polymerization and stereoregularities, *i.e.*, *cis*-transoidal and helical structures.[26−29] In this paper, we synthe-
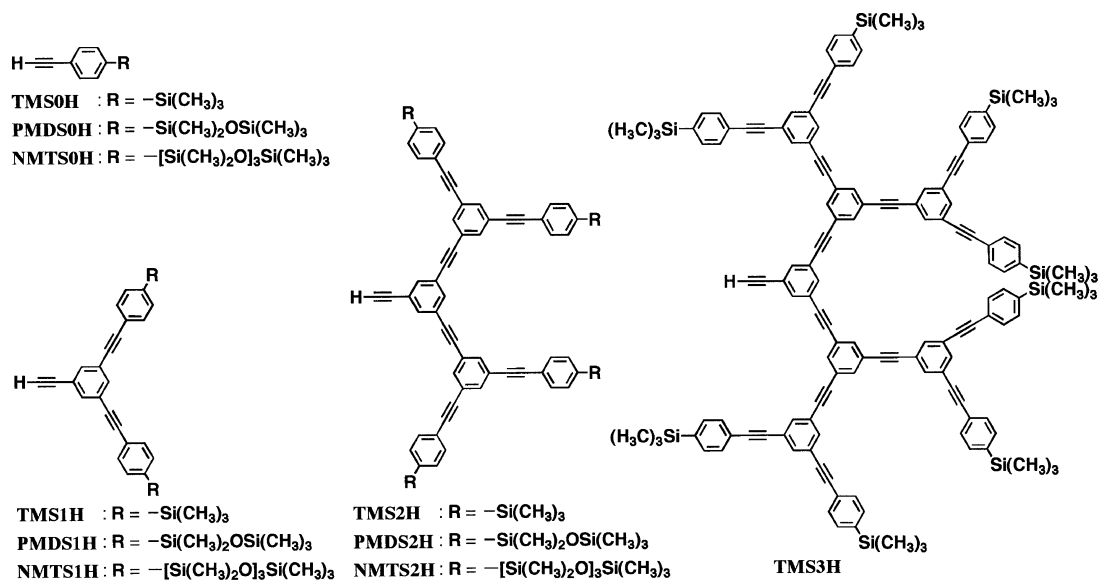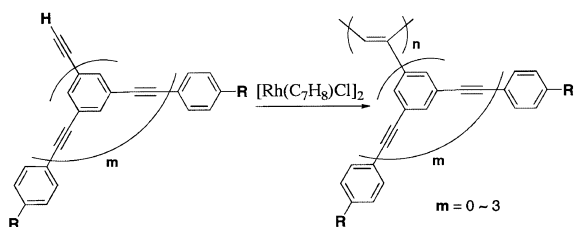
Scheme 1.

Scheme 2.

sized monodendrons, as shown in Scheme 1, consisting of *m*-linked phenyleneethynylene repeating unit with trimethylsilyl- (**TMS**), pentamethyldisiloxanyl- (**PMDS**), and nonamethyltetrasiloxanyl- (**NMTS**) peripheral groups which are flexible peripheral groups to afford adequate solvent solubility, and polymerized the monodendron monomers by a rhodium complex catalyst as shown in Scheme 2. The resulting polydendrons were characterized using ^{1}H NMR, ^{13}C NMR, XRD, SFM, GPC-LALLS, and other experiment of instruments.

RESULTS AND DISCUSSION

Synthesis of Monodendrons

It is well known that a phenyleneethynylene structure is prepared by the well-established and high-yielding palladium-catalyzed cross-coupling reaction of terminal acetylenes and arylhalides.[30] Moore *et al.*, synthesized dendrimers consisting of *m*-linked phenyleneethynylene repeating unit up to fourth generation by convergent method using the palladium-catalyzed cross-coupling reaction, trimethylsilyl group as a protecting group for terminal acetylenes, and 1-aryl-3,3-dialkyltriazenes as masking groups for the aryl iodide bond.[31] We also synthesized new monodendrons

consisting of phenyleneethynylene repeating unit up to third generation as shown in Scheme 3 by repetition of the coupling reaction of 3,5-dihalogeno-1-(3-hydroxy-3-methylbutynyl)benzene with the phenylacetylene derivatives of earlier generation and the elimination reaction of terminal acetylene-protecting group, where 1-hydroxyl-1-methylethyl group was employed as a protecting group for terminal acetylenes because the hydroxyl group of the protecting group was effective for following column separation. The length of the peripheral group did not affect coupling yield, while the yield decreased with generation of the dendrons. But the coupling yield was improved by using 3,5-diiodo-1-(3-hydroxy-3-methylbutynyl)benzene as the focal unit instead of 3,5-dibromo-1-(3-hydroxy-3-methylbutynyl)benzene. For example, the third generation **TMS3H** was obtained by coupling reaction of 3,5-diiodo-1-(3-hydroxy-3-methylbutynyl)benzene with **TMS2H**, although it was not obtained by 3,5-dibromo-1-(3-hydroxy-3-methylbutynyl)benzene. The chemical structures of the monodendron monomers were confirmed by means of ^{1}H NMR, ^{13}C NMR and IR spectra. **TMS** series of the monodendrons were amorphous solid, while **PMDS** and **NMTS** series were viscous compounds owing to the effect of flexible siloxane chain as the peripheral group.

Polymerization of Monodendron Monomers

The monodendron monomers were polymerized by rhodium catalyst, $[Rh(C_7H_8)Cl]_2$, with triethylamine co-catalyst, and the polymerization mixtures were purified by precipitating into methanol or methanol/benzene (3/2 v/v) to yield the corresponding polydendrons as yellow powders. The rhodium
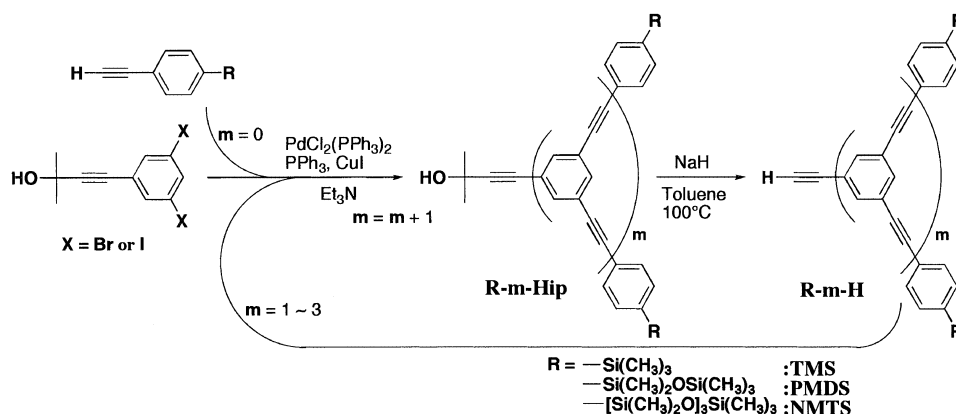
Scheme 3.

catalyst can selectively polymerize monosubstituted acetylenes,[32, 33] while Mo and W catalysts polymerize not only monosubstituted but also disubstituted acetylenes.[34] Therefore, the rhodium catalyst was found to be more effective for polymerization of the monodendrons only at the terminal acetylene group of focal point. The characterization performed by means of IR, ^{1}H NMR, and ^{13}C NMR allowed this statement; for example, in IR, ^{1}H NMR, and ^{13}C NMR spectra of poly(**TMS1H**), the peaks assignable to the terminal acetylene group of the monodendron **TMS1H**, *i.e.*, 3312 cm^{-1} (the stretching vibration of the ≡C–H bond) in IR spectrum, δ 3.12 (s, 1 H, ≡C–H) in ^{1}H NMR, and δ 78.30 and 82.04 in ^{13}C NMR, completely disappeared with retaining those of the inner acetylene groups, *i.e.*, δ 89.61 and 90.28 in ^{13}C NMR (Figure 1).

The polydendrons showed high solubility, and had a high degree of polymerization ($\overline{DP} > 10^3$) under the polymerization conditions as shown in Table I. However, the yield and degree of polymerization decreased as the increment of generation in the same polymerization conditions (*e.g.*, $[Cat]_0/[M]_0 = 1/500$). The polymerization of **TMS3H** was particularly inhibited because the terminal acetylene was probably hidden by dendritic moieties. The solubility of the monodendrons and polydendrons preferred toluene to chloroform due to aromatic structure of the dendrons. Therefore, the polymerization in toluene resulted in a better yield and a higher degree of polymerization compared to those in chloroform. **PMDS1H** and **NMTS1H** also gave highly soluble polydendrons with a high degree of polymerization ($\overline{DP} > 10^3$) in spite of the larger peripheral groups in comparison with **TMS1H**, although the polymerization of **PMDS2H** and **NMTS2H** resulted in a reduced yield and degree of polymerization due to the steric crowding of peripheral group as well as that of **TMS3H** (Table II). The polydendrons showed good film-forming property depending on their degree of polymerization, and gave a self-supporting
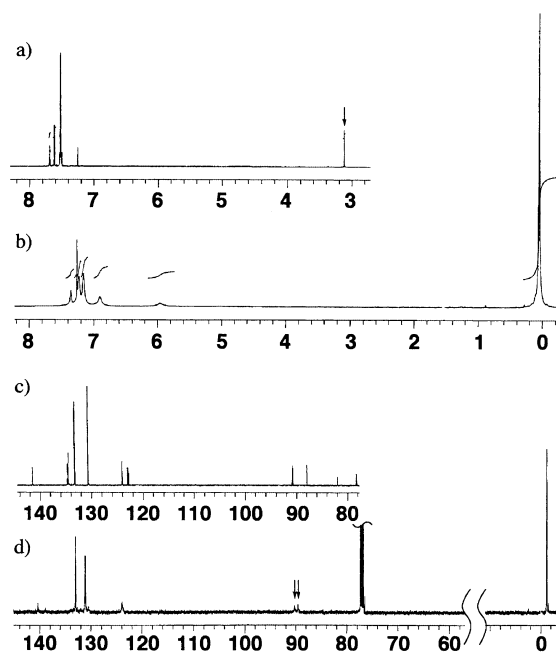
Figure 1. ^{1}H NMR (500 MHz) spectra of a) **TMS1H** and b) poly(**TMS1H**), and ^{13}C NMR spectra of c) **TMS1H** and d) poly(**TMS1H**).

film with orange color due to π-conjugated main-chain chromophore by the solvent-casting method.

Structure of Polydendrons

By using ^{1}H NMR spectroscopy it is possible for poly(phenylacetylene)s to analyze the *cis–trans* microstructure of the main-chain.[35] In ^{1}H NMR of the polydendrons, the peak at δ 5.8–6.0 assignable to *cis* proton of poly(phenylacetylene) main-chain supported that the *cis* content of the polymer was high.[36]

Figure 2 shows plots of the ratio of the logarithmic $\overline{M}_n$ or $\overline{M}_w$ of the polydendrons of **TMS** series from GPC calibrated with polystyrene standard to the logarithmic $\overline{M}_n$ or $\overline{M}_w$ from GPC-LALLS (log M(RI)/log M(LS)) *vs.* the molecular weight of the monomers, monodendrons. $\overline{M}_w$s from polystyrene standard are smaller than those from GPC-LALLS. This tendency

Table I. Polymerization of phenylacetylene monodendrons with trimethylsilyl peripheral groups using $[Rh(C_7H_8)Cl]_2$

| Monomers	Generation number	Solv.	$\dfrac{[M]_0}{[Cat]_0}$	$\dfrac{Yield}{\%}$	$\dfrac{\overline{M}_w{}^c}{\times 10^6}$	$\overline{M}_w/\overline{M}_n{}^c$	$\dfrac{\overline{DP}{}^d}{\times 10^3}$
TMS0H[a]	0	CHCl$_3$	100	92	1.2	2.5	6.9
			200	92	1.3	1.7	7.6
TMS1H[a]	1	CHCl$_3$	500	83	2.5	1.4	5.7
		Toluene	500	87	4.0	1.4	8.9
			2500	86	3.1	1.3	6.9
TMS2H[a]	2	CHCl^3	500	50	1.6	2.0	1.6
			2500	26	2.8^e	1.4	2.8
			5000	36	0.11	3.7	0.11
		Toluene	5000	83	1.9	4.6	1.9
			50000	10	0.59	5.1	0.60
TMS3H[b]	3	Toluene	50	65	0.040	1.3	0.020
			500	0.8	0.13	2.2	0.064

[a]$[M]_0 = 0.5$ mol L^{-1}, [triethylamine]$_0$/[Cat]$_0 = 20$, 25°C, 3 h, precipitated with MeOH/benzene (3/2, v/v). [b]$[M]_0 = 0.3$ mol L^{-1}, [triethylamine]$_0$/[Cat]$_0 = 20$, 25°C, 3 h, precipitated with MeOH. [c]Determined from GPC-LALLS. [d]Calculated from $\overline{M}_w$. [e]Soluble part.

Table II. Polymerization of phenylacetylene monodendrons with oligo(dimethylsiloxane) chains as peripheral groups using $[Rh(C_7H_8)Cl]_2{}^a$

Monomers	Generation number	$\dfrac{[M]_0}{[Cat]_0}$	$\dfrac{Yield}{\%}$	$\dfrac{\overline{M}_w{}^b}{\times 10^6}$	$\overline{M}_w/\overline{M}_n{}^b$	$\dfrac{\overline{DP}{}^c}{\times 10^3}$
PMDS0H	0	5000	58	0.76	1.9	3.1
NMTS0H	0	5000	30	1.3	1.7	3.2
PMDS1H	1	5000	88	2.5	1.7	4.2
NMTS1H	1	500	94	4.2	1.6	4.7
		5000	92	3.4	1.7	3.9
PMDS2H	2	5000	8	0.43	2.2	0.34
NMTS2H	2	500	42	0.08	2.2	0.04
		5000	4	0.30	4.0	0.16

[a]Toluene, [TEA]$_0$/[Cat]$_0 = 20$, 25°C, 2h, precipitated with MeOH. [b]Determined from GPC-LALLS. [c]Calculated from $\overline{M}_w$.
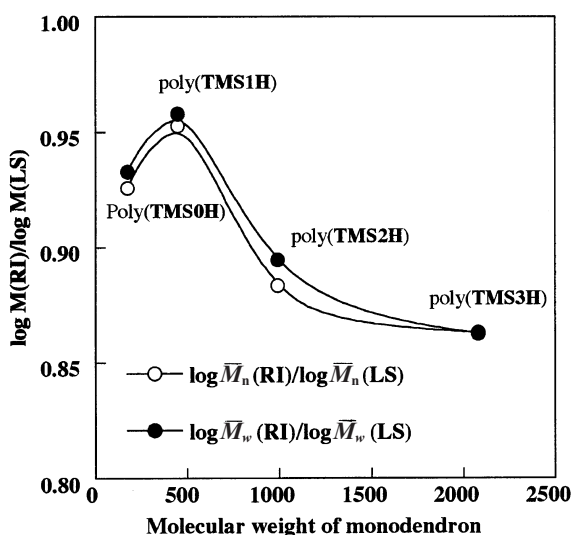
Figure 2. Dependence of $\overline{M}_n$ or $\overline{M}_w$ (RI) calibrated with PSt standard *vs.* $\overline{M}_n$ or $\overline{M}_w$ (LS) determined from GPC-LALLS for polydendrons.

becomes more remarkable with increase of the generation, which indicates that the dendritic structure re-

tained a very compact molecular size in the solution, as was observed in the case of other dendrimers.[1] Other types of polydendrons also showed the same tendency.

The visible absorption spectra of polydendrons are shown in Figure 3. A bathochromic shift has been reported for some *ortho-* and *meta-* substituted poly-(phenylacetylene)s in comparison with the simple or *para*-substituted poly(phenylacetylene).[34, 37] The visible absorption maxima (λ_{max}) of the first and second generation polydendrons also significantly increase due to effect of the bulky substituent at *m*-position in comparison with the corresponding zero generation polymer poly(**TMS0H**). This bathochromic shift indicates a developed π-conjugation in the main-chain of polydendrons, and suggests that steric hindrance and repulsion among bulky substituents at *m*-position formed the extended main-chain structure and the crowded side-chain structure, and resulted in a highly twisted dihedral angle between main-chain and the attached phenyl rings, and, counteractingly, slightly or moderately twisted single bonds of main-chain. Recent com-

Table III. Columun structure of polydendrons

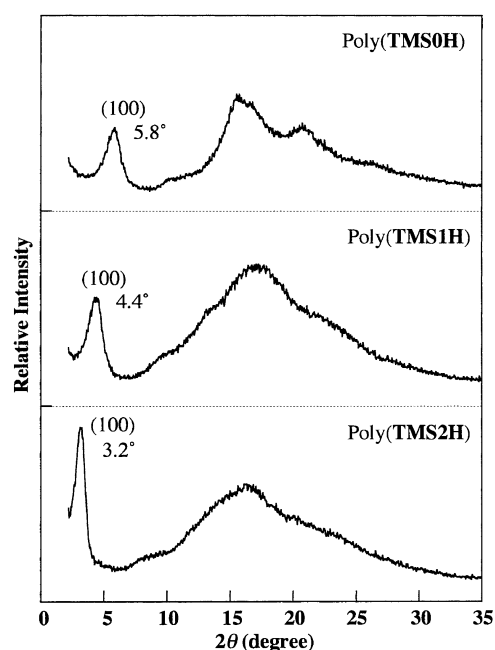| Polymers	Generation number	Density[a] g cm^{-3}	2θ[b] deg	d spacing[c] Å	Column diameter WAXS[d] (Å)	Calcd[e] (Å)
poly(**TMS0H**)	0	0.962	5.8	15.2	17.6	16.2
poly(**TMS1H**)	1	1.008	4.4	20.1	23.2	25.0
poly(**TMS2H**)	2	1.027	3.2	27.6	31.9	35.2
poly(**TMS3H**)[f]	3					44.9
poly(**PMDS0H**)	0	0.988[g]	5.2	17.0	19.6	20.4
poly(**PMDS1H**)	1	1.019	4.0	22.1	25.5	29.4
poly(**PMDS2H**)[f]	2					50.6
poly(**NMTS0H**)	0	>1[g]	4.3	20.5	23.7	28.8
poly(**NMTS1H**)	1	1.014	3.2	27.6	31.9	39.1
poly(**NMTS2H**)[f]	2	1.031				60.2

[a]Determined by floating method containing error of 0.005. [b]Crystalline peak of the wide-angle X-Ray scattering (WAXS) of the polymers. [c]Estimated from 2θ. [d]Estimated from d (Column diameter $= 2d/\sqrt{3}$). [e]Estimated from molecular modeling which was performed as described in note 41. [f]The sample was not obtained enough for the WAXS experiment. [g]From ref 43.
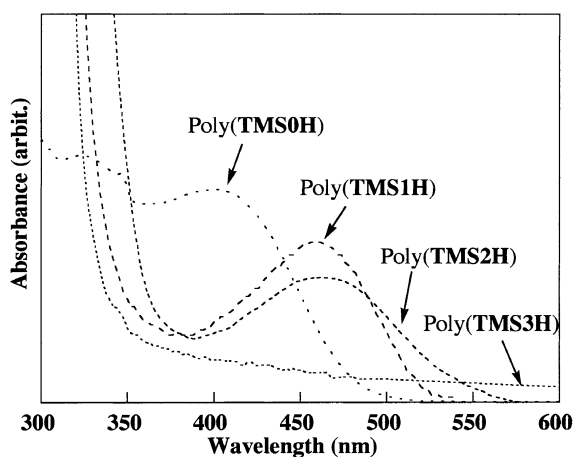
Figure 3. Visible absorption spectra of polydendrons with trimethylsilyl peripheral group in chloroform.

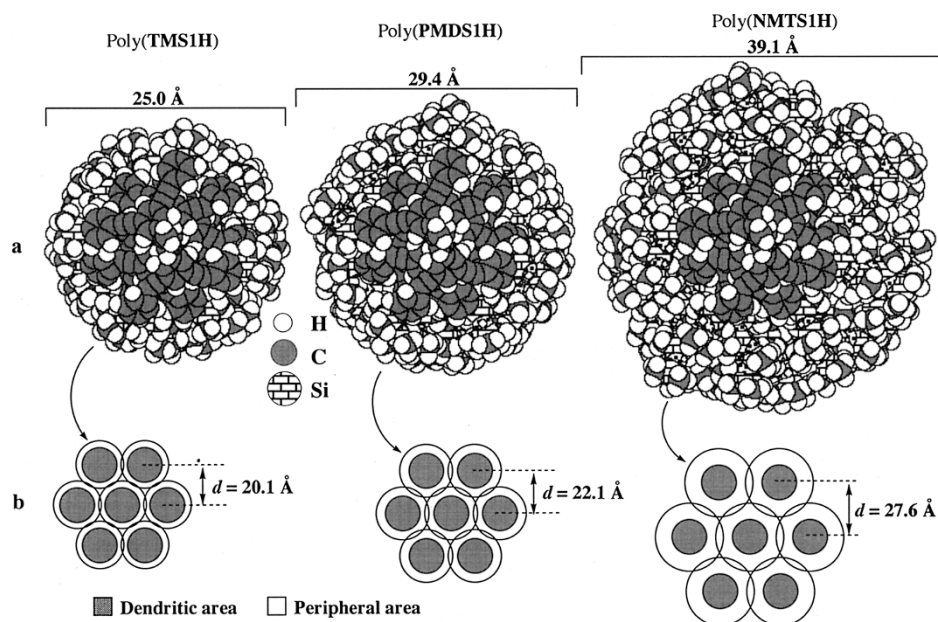**Figure 4.** WAXS patterns of poly(**TMS0H**), poly(**TMS1H**), and poly(**TMS2H**).

putational studies of poly(phenylacetylene) derivatives also support that the energetically preferred conformation was the slightly distorted *cis*-transoid and/or helical main-chain structure with the large phenyl–C=C dihedral twisting angle.[28, 38, 39] The third generation polydendron poly(**TMS3H**) has no absorption maxima in the visible range due to the further bulky side-chain dendrons.

The wide angle X-Ray scattering (WAXS) of the polydendrons was measured in film states, and the WAXS patterns of poly(**TMS0H**), poly(**TMS1H**) and poly(**TMS2H**) are shown in Figure 4. The sharp peaks are observed at $2\theta = 3$–$6°$ besides a broad amorphous halo at $2\theta = 10$–$30°$. These sharp crystalline peaks are attributed to the (100) reflection of the pseudohexagonal lattice of rod-like molecules.[11, 26, 40] Table III summarizes the result of WAXS experiments of polydendrons. The interplanar d spacing of **TMS** series increase with increasing generation, while the density also increased. These experimental facts suggest that the increase of d spacing is related to the increase of the column diameter with increasing generation. The column diameter of **TMS** series estimated from d spacing is only slightly smaller than that of molecular modeling[41] except for poly(**TMS0H**). The difference of poly(**TMS0H**) from other **TMS** series can be explained from the cone-angle of the side-chain, *i.e.*, the distorted main-chain of poly(**TMS0H**) extends the cone-angle from 60° calculated from *cis*-transoid main-chain conformation, and/or from the loosely packing of the polymer chain. This consideration agreed with the results of visible absorption described above and the comparatively broad WAXS peak of poly(**TMS0H**). The interplanar d spacing of polydendrons also increase with the length of the peripheral group. However, the column

Poly(TMS1H) 25.0 Å

Poly(PMDS1H) 29.4 Å

Poly(NMTS1H) 39.1 Å

○ H
● C
⊞ Si

a

b

d = 20.1 Å   *d* = 22.1 Å   *d* = 27.6 Å

▨ Dendritic area   ☐ Peripheral area

Figure 5. (a) Top view of space-filling models along the polymer chain, and (b) schematic drawing of column structure estimated from WAXS for polydendrons with oligodimethylsiloxyanyl peripheral group.

diameter difference between the values estimated from *d* spacing and from molecular modeling increases with the length of the peripheral group, which suggests that the flexible siloxane chain as the peripheral group was bent, and/or the columns slightly overlapped each other in the part of the peripheral group as shown in Figure 5.

Atomic force microscopy (AFM) image of the polydendrons also supported the structure of polydendrons. Figure 6 depicts AFM images of **TMS** series of polydendrons prepared on mica by spin casting of dilute chloroform solution. The AFM images indicates the formation of monolayer for the most part. From cross sectional profiles **a** and **b** in Figure 6, the monolayer thickness of poly(**TMS1H**) and poly(**TMS2H**) are determined to be 2.7 and 3.6 nm, respectively. These values correspond to the column diameter determined from WAXS experiments. Additionally, in the minority multilayer part, the height difference between successive layers agree with the *d* spacing at (100) surface as shown in cross sectional profiles **a** and **c** in Figure 6.

CONCLUSIONS

We synthesized novel phenylacetylene monomers consisting of dendrimer with a phenyleneethynylene repeating unit. The monodendron monomers were successfully polymerized with a rhodium catalyst, [Rh(C₇H₈)Cl]₂, to give the corresponding polydendrons with high molecular weight in spite of their bulky dendritic residue up to the third generation, though the yield and degree of polymerization decreased as increment of generation. This good ability of the poly-

merization was attained because the shape-persistency or planarity of the monomers facilitated the reasonable packing of the bulky side-chain in polymerization. The polydendrons were fabricated to self-supporting membranes, and would be available for providing the materials with unique function such as oxygen-permselective membrane. It is beyond the scope of this paper to discuss the subject in further detail.

EXPERIMENTAL

Materials

[4-(Trimethylsilyl)phenyl]acetylene (**TMS0H**),[42] [4-(pentamethyldisiloxanyl)phenyl]acetylene (**PMDS0H**)[43], and [4-(nonamethyltetrasiloxanyl)phenyl]acetylene (**NMTS0H**),[43] were synthesized as previously described. (Bicyclo[2.2.1]hepta-2,5-diene)chlororhodium(I) dimer catalyst ([Rh(C₇H₈)Cl]₂) (Aldrich Chemical Co.), bis(triphenylphosphine)palladium(II) chloride (Aldrich Chemical Co.), and *n*-butyllithium (Kanto Chemical Co., Inc., 1.6 M in hexane) were used without further purification. Other conventional reagents were used as received or purified by conventional method.

Synthesis of Monomers

3,5-Dibromo-1-(3-hydroxy-3-methylbutynyl)benzene. 2-methyl-3-butyn-2-ol (3.9 mL, 40 mmol) was added to a triethylamine/pyridine solution (60 mL/ 40 mL) of 1,3,5-tribromobenzene (12 g, 40 mmol), bis(triphenylphosphine)palladium(II) chloride (83 mg, 0.12 mmol), triphenylphosphine (160 mg, 0.62 mmol)
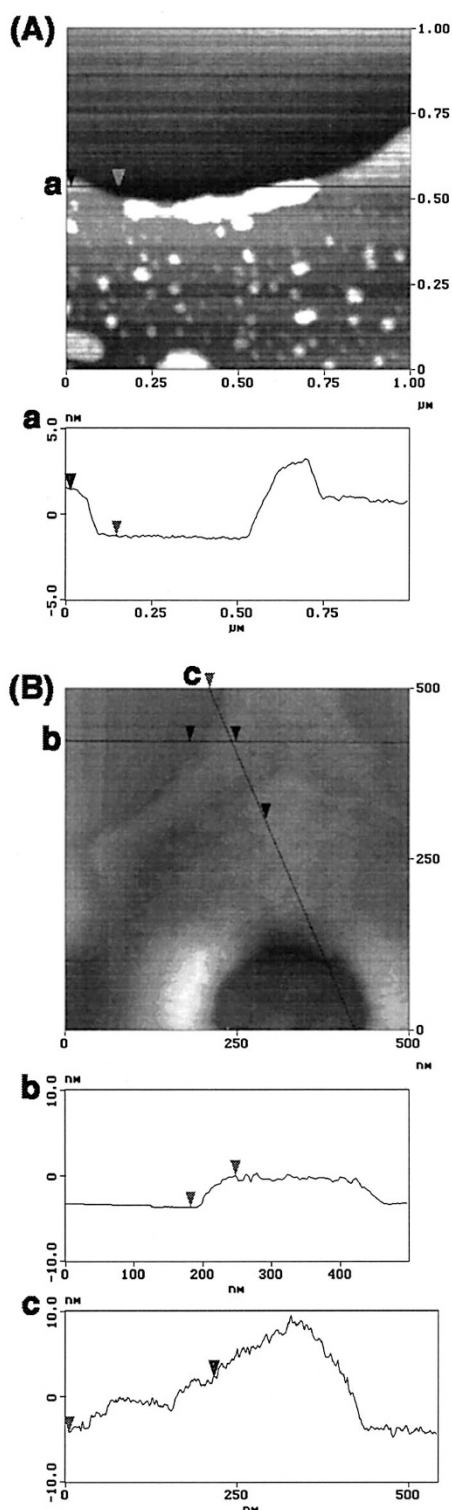
Figure 6. AFM images and cross sectional height profiles of (A) poly(**TMS1H**) and (B) poly(**TMS2H**) prepared by spincasting of 0.05 mg mL^{-1} solutions in chloroform onto mica substrate.

and copper (I) iodide (82 mg, 0.43 mmol) under a nitrogen atmosphere. The solution was stirred and refluxed for 18 h to give triethylamine bromide precipitate. The mixture was filtered off, and the filtrate was evaporated, then extracted with chloroform, and washed with water. The organic layer was dried over anhydrous sodium sulfate, and the solvent was re-

moved under reduced pressure. The residue was dissolved in diethyl ether, and washed with 10% HCl. The ether layer was dried over anhydrous sodium sulfate, and the solvent was evaporated. The residue was dissolved in benzene (150 mL), and ethylene diamine (30 mL) was added to the solution. The solution was heated at 80°C for 20 min. After cooling, the mixture was filtered off, and the filtrate was washed with 10% HCl and water, and dried over anhydrous sodium sulfate. The solvent was evaporated, and the crude product was purified by silica-gel column separation with dichloromethane as an eluent to give 3,5-dibromo-1-(3-hydroxy-3-methylbutynyl)benzene (10 g, 33 mmol). Yield 82% . TLC (dichloromethane): R_f = 0.43. IR (NaCl; cm^{-1}): 3364 (ν_{O-H}), 2988 (ν_{C-H}). ^{1}H NMR (CDCl$_3$, 200 MHz; ppm): δ 1.60 (s, 6H, CH$_3$), 2.09 (s, 1H, –OH), 7.49 (d, 2H, J = 1.7 Hz, ArH), 7.60 (t, 1H, J = 1.7 Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 31.28, 65.52, 79.34, 96.39, 122.52, 126.13, 133.08, 133.98.

3,5-Diiodo-1-(3-hydroxy-3-methylbutynyl)benzene. 2-Methyl-3-butyn-2-ol (0.18 mL, 1.9 mmol) was added to a triethylamine/pyridine solution (12 mL/8 mL) of 1,3,5-triiodobenzene (0.8 g, 1.8 mmol), bis(triphenylphosphine)palladium(II) chloride (8.2 mg, 0.012 mmol), triphenylphosphine (12 mg, 0.055 mmol) and copper (I) iodide (7.4 mg, 0.038 mmol) under a nitrogen atmosphere. The solution was stirred for 18 h at 50°C. The mixture was worked up in the same manner as described above, and the crude product was purified by silica-gel column separation with dichloromethane as an eluent to give 3,5-diiodo-1-(3-hydroxy-3-methylbutynyl)benzene (0.33 g, 0.8 mmol). Yield 45%. TLC (dichloromethane): R_f = 0.41. IR (NaCl; cm^{-1}): 3372 (–OH), 2988 (C–H). ^{1}H NMR (CDCl$_3$, 200 MHz; ppm): δ 1.59 (s, 6H, CH$_3$), 1.99 (s, 1H, –OH), 7.72 (d, 2H, J = 1.4 Hz, ArH), 7.99 (t, 1H, J = 1.4 Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 31.20, 65.37, 78.83, 94.01, 96.34. 126.13, 139.23, 144.63.

TMS1Hip. A triethylamine (65 mL) solution of 3-5-dibromo-1-(3-hydroxy-3-methylbutynyl)benzene (4.1 g, 13 mmol), **TMS0H** (5.0 g, 29 mmol), bis(triphenylphosphine)palladium(II) chloride (91 mg, 0.13 mmol), triphenylphosphine (85 mg, 0.33 mmol) and copper (I) iodide (85 mg, 0.44 mmol) was stirred for 18 h at 95°C under a nitrogen atmosphere. The mixture was worked up in the same manner as described above, and the crude product was purified by silica-gel column separation with hexane/dichloromethane (1/4) as an eluent to give **TMS1Hip** (6.0 g, 12 mmol). Yield 92%. TLC (hexane/CHCl$_3$ = 1/4): R_f = 0.54. IR (KBr; cm^{-1}): 3400 (–OH), 2964 (C–H), 2216 (C≡C), 1252 (Si–C). ^{1}H NMR (CDCl$_3$, 200 MHz; ppm): δ 0.28 (s, 18H, Si(CH$_3$)$_3$), 1.62 (s, 6H, CH$_3$), 1.88 (s,

1H, OH), 7.50 (b, 8H, ArH), 7.54 (d, 2H, $J = 1.6\,\text{Hz}$, ArH), 7.63 (t, 1H, $J = 1.6\,\text{Hz}$, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ −1.25, 31.40, 64.57, 80.71, 88.11, 90.67, 94.91, 123.01, 123.45, 123.99, 130.71, 133.25, 134.11, 141.54.

TMS1H. Sodium hydride (0.26 g, 6.5 mmol) was added to a toluene solution (13 mL) of **TMS1Hip** (3.3 g, 6.5 mmol). The solution was heated to 100°C, and stirred for 2 h under a nitrogen flow. The reaction solution was washed with water, then dried over anhydrous sodium sulfate. The crude product was purified by silica-gel column separation with hexane as an eluent to give **TMS1H** (2.9 g, 6.5 mmol). Yield 100%; mp 89°C. TLC (hexane): $R_f = 0.36$. IR (NaCl; cm^{-1}): 3312 ($\equiv$C–H), 2964 (C–H), 2212 (C$\equiv$C), 1252 (Si–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.30 (s, 18H, Si(CH$_3$)$_3$), 3.12 (s, 1H, C$\equiv$C–H), 7.52 (d, 4H, $J = 8.3\,\text{Hz}$, ArH), 7.52 (d, 4H, $J = 8.3\,\text{Hz}$, ArH), 7.62 (d, 2H, $J = 1.5\,\text{Hz}$, ArH), 7.69 (t, 1H, $J = 1.5\,\text{Hz}$, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ −1.25, 78.30, 82.04, 87.96, 90.82, 122.82, 122.93, 124.08, 130.73, 133.26, 134.51, 134.67, 141.60. Anal. Calcd for (C$_{30}$H$_{30}$Si$_2$): C, 80.7; H, 6.8. Found: C, 80.5; H, 7.1.

TMS2Hip. A triethylamine (15 mL) solution of 3,5-dibromo-1-(3-hydroxy-3-methylbutynyl)benzene (0.81 g, 2.5 mmol), **TMS1H** (2.5 g, 5.6 mmol), bis-(triphenylphosphine)palladium(II) chloride (18 mg, 0.025 mmol), triphenylphosphine (16 mg, 0.063 mmol) and copper (I) iodide (16 mg, 0.085 mmol) was stirred for 18 h at 95°C under a nitrogen atmosphere. The mixture was worked up in the same manner as described above, and the crude product was purified by silica-gel column separation with hexane/dichloromethane (1/3) as an eluent to give **TMS2Hip** (1.8 g, 1.7 mmol). Yield 66%. TLC (hexane/CH$_2$Cl$_2$ = 1/3): $R_f = 0.66$. IR (KBr; cm^{-1}): 3400 (–OH), 2964 (C–H), 2220 (C$\equiv$C), 1252 (Si–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.29 (s, 36H, Si(CH$_3$)$_3$), 1.64 (s, 6H, CH$_3$), 2.04 (s, 1H, OH), 7.52 (d, 8H, $J = 8.0\,\text{Hz}$, ArH), 7.52 (d, 8H, $J = 8.0\,\text{Hz}$, ArH), 7.57 (d, 2H, $J = 1.8\,\text{Hz}$, ArH), 7.63 (t, 1H, $J = 1.8\,\text{Hz}$, ArH), 7.65 (d, 4H, $J = 1.5\,\text{Hz}$, ArH), 7.69 (t, 2H, $J = 1.5\,\text{Hz}$, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ −1.25, 31.39, 65.60, 80.51, 88.04, 88.68, 89.06, 90.84, 95.18, 122.96, 123.43, 123.59, 123.67, 124.17, 130.73, 133.27, 134.07, 134.17, 134.46, 134.49, 141.60.

TMS2H. **TMS2Hip** (1.7 g, 1.6 mmol) allowed to react with sodium hydride in the same manner as described above. The crude product was purified by silica-gel column separation with hexane/dichloromethane (1/1) as an eluent to give **TMS2H** (1.3 g, 1.3 mmol). Yield 80%. TLC (hexane/CHCl$_3$ = 1/1): $R_f = 0.93$. IR (KBr; cm^{-1}): 3316 ($\equiv$C–

H), 2964, 2932, 2856 (C–H), 2216 (C$\equiv$C), 1252 (Si–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.29 (s, 36H, Si(CH$_3$)$_3$), 3.15 (s, 1H, C$\equiv$C–H), 7.52 (s, 16H, ArH), 7.63 (d, 2H, $J = 1.5\,\text{Hz}$, ArH), 7.66 (d, 4H, $J = 1.5\,\text{Hz}$, ArH), 7.67 (t, 1H, $J = 1.5\,\text{Hz}$, ArH), 7.69 (t, 2H, $J = 1.5\,\text{Hz}$, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ −1.25, 78.63, 81.82, 88.04, 88.52, 89.21, 90.86, 122.96, 123.06, 123.37, 123.70, 124.18, 130.73, 133.27, 134.08, 134.50, 134.74, 134.88, 141.60. Anal. Calcd for (C$_{68}$H$_{62}$Si$_4$): C, 82.4; H, 6.3. Found: C, 82.9; H, 6.5.

TMS3Hip. A triethylamine (20 mL) solution of 3,5-diiodo-1-(3-hydroxy-3-methylbutynyl)benzene (0.23 g, 0.56 mmol), **TMS2H** (1.2 g, 1.2 mmol), bis(triphenylphosphine)palladium(II) chloride (3.9 mg, 0.0056 mmol), triphenylphosphine (3.6 mg, 0.014 mmol) and copper (I) iodide (3.6 mg, 0.019 mmol) was stirred for 15 h at 50°C under a nitrogen atmosphere. The mixture was worked up in the same manner as described above, and the crude product was purified by silica-gel column separation with hexane/dichloromethane (1/3) as an eluent to give **TMS3Hip** (1.0 g, 0.47 mmol). Yield 84%. TLC (hexane/CH$_2$Cl$_2$ = 1/3): $R_f = 0.60$. IR (NaCl; cm^{-1}): 3400 (–OH), 2968 (C–H), 2220 (C$\equiv$C), 1254 (Si–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.27 (s, 72H, Si(CH$_3$)$_3$), 1.64 (s, 6H, CH$_3$), 2.07 (s, 1H, OH), 7.50 (s, 32H, ArH), 7.58 (d, 2H, $J = 1.5\,\text{Hz}$, ArH), 7.65 (t, 1H, $J = 1.5\,\text{Hz}$, ArH), 7.65 (d, 8H, $J = 1.5\,\text{Hz}$, ArH), 7.65 (d, 4H, $J = 1.5\,\text{Hz}$, ArH), 7.66 (t, 2H, $J = 1.5\,\text{Hz}$, ArH), 7.68 (t, 4H, $J = 1.5\,\text{Hz}$, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ −1.25, 31.40, 65.59, 80.50, 88.06, 88.65, 88.86, 88.97, 89.28, 90.86, 95.24, 122.97, 123.40, 123.53, 123.67, 123.70, 123.80, 124.19, 130.75, 133.26, 134.10, 134.41, 134.50, 134.67, 141.57.

TMS3H. **TMS3Hip** (0.95 g, 0.44 mmol) allowed to react with sodium hydride in the same manner as described above. The crude product was purified by silica-gel column separation with chloroform as an eluent to give **TMS3H** (0.83 g, 0.40 mmol). Yield 90%. TLC (CHCl$_3$): $R_f = 0.90$. IR (KBr; cm^{-1}): 3305 ($\equiv$C–H), 2964 (C–H), 2220 (C$\equiv$C), 1252 (Si–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.27 (s, 72H, Si(CH$_3$)$_3$), 3.15 (s, 1H, C$\equiv$C–H), 7.50 (s, 32H, ArH), 7.64 (d, 2H, $J = 1.8\,\text{Hz}$, ArH), 7.65 (d, 8H, $J = 1.5\,\text{Hz}$, ArH), 7.66 (d, 4H, $J = 1.5\,\text{Hz}$, ArH), 7.67 (t, 2H, $J = 1.5\,\text{Hz}$, ArH), 7.68 (t, 4H, $J = 1.5\,\text{Hz}$, ArH), 7.69 (t, 1H, $J = 1.8\,\text{Hz}$, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ −1.25, 78.71, 81.80, 88.05, 88.64, 88.81, 89.00, 89.29, 90.86, 122.96, 123.10, 123.40, 123.62, 123.64, 123.81, 124.19, 130.74, 133.26, 134.10, 134.43, 134.49, 134.58, 134.66, 135.06, 141.57. Anal. Calcd for (C$_{144}$H$_{126}$Si$_8$): C, 83.1; H, 6.1. Found: C, 83.2; H,

6.2.

PMDS1Hip. 3,5-Dibromo-1-(3-hydroxy-3-methyl-butynyl)benzene (3.2 g, 10 mmol) was allowed to react with **PMDS0H** (5.6 g, 22 mmol) in the same manner as described above. The crude product was purified by silica-gel column separation with chloroform as an eluent to give **PMDS1Hip** (5.7 g, 8.5 mmol). Yield 85%. TLC (CHCl$_3$): R_f = 0.57. IR (NaCl; cm^{-1}): 3364 (–OH), 2968 (C–H), 2216 (C≡C), 1260 (Si–C). ^{1}H NMR (CDCl$_3$, 200 MHz; ppm): δ 0.10 (s, 18H, Si(CH$_3$)$_3$), 0.34 (s, 12H, Si(CH$_3$)$_2$), 1.63 (s, 6H, CH$_3$), 2.18 (s, 1H, OH), 7.52 (d, 4H, J = 8.2 Hz, ArH), 7.53 (d, 4H, J = 8.2 Hz, ArH), 7.55 (d, 2H, J = 1.8 Hz, ArH), 7.65 (t, 1H, J = 1.8 Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 0.78, 1.94, 31.40, 65.54, 80.68, 88.21, 90.68, 94.98, 123.40, 123.49, 123.98, 130.72, 132.91, 134.12, 141.07.

PMDS1H. **PMDS1Hip** (5.7 g, 8.9 mmol) allowed to react with sodium hydride in the same manner as described above. The crude product was purified by silica-gel column separation with hexane/dichloromethane (1/1) as an eluent to give **PMDS1H** (4.5 g, 7.7 mmol). Yield 87%. TLC (hexane/CH$_2$Cl$_2$ = 1/1): R_f = 0.82. IR (NaCl; cm^{-1}): 3316 (≡C–H), 2964 (C–H), 2216 (C≡C), 1258 (Si–C). ^{1}H NMR (CDCl$_3$, 200 MHz; ppm): δ 0.10 (s, 18H, Si(CH$_3$)$_3$), 0.34 (s, 12H, Si(CH$_3$)$_2$), 3.12 (s, 1H, C≡C–H), 7.53 (d, 4H, J = 8.3 Hz, ArH), 7.53 (d, 4H, J = 8.3 Hz, ArH), 7.62 (d, 2H, J = 1.5 Hz, ArH), 7.69 (t, 1H, J = 1.5 Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 0.80, 1.96, 78.31, 82.04, 88.05, 90.83, 122.87, 123.33, 124.10, 130.76, 132.94, 134.55, 134.69, 141.15. Anal. Calcd for (C$_{34}$H$_{42}$O$_2$Si$_4$): C, 68.6; H, 7.1. Found: C, 69.0; H, 6.9.

PMDS2Hip. 3,5-Dibromo-1-(3-hydroxy-3-methyl-butynyl)benzene (0.93 g, 3.0 mmol) was allowed to react with **PMDS1H** (3.9 g, 6.7 mmol) in the same manner as described above. The crude product was purified by silica-gel column separation with hexane/dichloromethane (1/1) as an eluent to give **PMDS2Hip** (1.9 g, 1.5 mmol). Yield 50%. TLC (hexane/CH$_2$Cl$_2$ = 1/1): R_f = 0.41. IR (NaCl; cm^{-1}): 3368 (–OH), 2964 (C–H), 2220 (C≡C), 1256 (Si–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.10 (s, 36H, Si(CH$_3$)$_3$), 0.34 (s, 24H, Si(CH$_3$)$_2$), 1.65 (s, 6H, CH$_3$), 2.03 (s, 1H, OH), 7.53 (d, 8H, J = 8.0 Hz, ArH), 7.55 (d, 8H, J = 8.0 Hz, ArH), 7.58 (d, 2H, J = 1.5 Hz, ArH), 7.64 (t, 1H, J = 1.5 Hz, ArH), 7.66 (d, 4H, J = 1.5 Hz, ArH), 7.69 (t, 2H, J = 1.5 Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 0.80, 1.96, 31.40, 65.60, 80.51, 88.14, 88.70, 89.05, 90.86, 95.19, 123.34, 123.45, 123.59, 123.67, 124.16, 130.75, 132.94, 134.10, 134.17, 134.47, 134.51, 141.14.

PMDS2H. **PMDS2Hip** (1.3 g, 1.0 mmol) allowed to react with sodium hydride in the same manner

as described above. The crude product was purified by silica-gel column separation with hexane/dichloromethane (4/1) as an eluent to give **PMDS2H** (0.87 g, 0.67 mmol). Yield 67% ; mp 127°C. TLC (hexane/CH$_2$Cl$_2$ = 4/1): R_f = 0.40. IR (NaCl; cm^{-1}): 3316 (≡C–H), 2964 (C–H), 2216 (C≡C), 1258 (Si–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.10 (s, 36H, Si(CH$_3$)$_3$), 0.34 (s, 24H, Si(CH$_3$)$_2$), 3.15 (s, 1 H, C≡C–H), 7.53 (d, 8H, J = 8.0 Hz, ArH), 7.55 (d, 8H, J = 8.0 Hz, ArH), 7.63 (d, 2H, J = 1.5 Hz, ArH), 7.66 (d, 4H, J = 1.5 Hz, ArH), 7.68 (t, 1H, J = 1.5 Hz, ArH), 7.69 (t, 2H, J = 1.5 Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 0.80, 1.96, 78.65, 81.83, 88.13, 88.54, 89.21, 90.88, 123.10, 123.35, 123.41, 123.72, 124.20, 130.76, 132.94, 134.12, 134.53, 134.76, 134.92, 141.16. Anal. Calcd for (C$_{76}$H$_{86}$O$_4$Si$_8$): C, 70.9; H, 6.7. Found: C, 70.9; H, 6.3.

NMTS1Hip. 3,5-Dibromo-1-(3-hydroxy-3-methyl-butynyl)benzene (1.6 g, 5.2 mmol) was allowed to react with **NMTS0H** (4.5 g, 11 mmol) in the same manner as described above. The crude product was purified by silica-gel column separation with chloroform as an eluent to give **NMTS1Hip** (3.2 g, 3.4 mmol). Yield 65%. TLC (CHCl$_3$): R_f = 0.60. IR (NaCl; cm^{-1}): 3356 (–OH), 2968 (C–H), 2220 (C≡C), 1264 (Si–C). ^{1}H NMR (CDCl$_3$, 200 MHz; ppm): δ 0.05 (s, 12H, Ph–Si–O–Si–O–Si(CH$_3$)$_2$), 0.08 (s, 12H, Ph–Si–O–Si(CH$_3$)$_2$), 0.10 (s, 18H, Si(CH$_3$)$_3$), 0.36 (s, 12H, Ph–Si(CH$_3$)$_2$), 1.64 (s, 6H, CH$_3$), 2.01 (s, 1H, OH), 7.51 (d, 4H, J = 8.2 Hz, ArH), 7.56 (d, 4H, J = 8.2 Hz, ArH), 7.56 (d, 2H, J = 1.8 Hz, ArH), 7.65 (t, 1H, J = 1.8 Hz, ArH).

NMTS1H. **NMTS1Hip** (3.2 g, 3.4 mmol) allowed to react with sodium hydride in the same manner as described above. The crude product was purified by silica-gel column separation with dichloromethane as an eluent to give **NMTS1H** (2.3 g, 2.6 mmol). Yield 75%. TLC (CH$_2$Cl$_2$): R_f = 0.94. IR (NaCl; cm^{-1}): 3316 (≡C–H), 2968 (C–H), 2216 (C≡C), 1264 (Si–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.03 (s, 12H, Ph–Si–O–Si–O–Si(CH$_3$)$_2$), 0.07 (s, 12H, Ph–Si–O–Si(CH$_3$)$_2$), 0.08 (s, 18H, Si(CH$_3$)$_3$), 0.35 (s, 12H, Ph-Si(CH$_3$)$_2$), 3.11 (s, 1 H, C≡C–H), 7.51 (d, 4H, J = 8.2 Hz, ArH), 7.55 (d, 4H, J = 8.2 Hz, ArH), 7.60 (d, 2H, J = 1.5 Hz, ArH), 7.68 (t, 1H, J = 1.5 Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 0.69, 1.16, 1.19, 1.81, 78.29, 82.02, 88.02, 90.82, 122.83, 123.32, 124.07, 130.71, 132.98, 134.54, 134.69, 140.87. Anal. Calcd for (C$_{42}$H$_{66}$O$_6$Si$_8$): C, 56.6; H, 7.5. Found: C, 56.6; H, 7.3.

NMTS2Hip. 3,5-Dibromo-1-(3-hydroxy-3-methyl-butynyl)benzene (0.51 g, 1.7 mmol) was allowed to react with **NMTS1 H** (3.2 g, 3.7 mmol) in the same manner as described above. The crude product

was purified by silica-gel column separation with hexane/dichloromethane (1/1) as an eluent to give **NMTS2Hip** (1.1 g, 0.57 mmol). Yield 34%. TLC (hexane/CH$_2$Cl$_2$ = 1/1): R_f = 0.46. IR (NaCl; cm^{-1}): 3420 (–OH), 2968 (C–H), 2224 (C≡C), 1262 (Si–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.04 (s, 24H, Ph–Si–O–Si–O–Si(CH$_3$)$_2$), 0.07 (s, 24H, Ph–Si–O–Si(CH$_3$)$_2$), 0.08 (s, 36 H, Si(CH$_3$)$_3$), 0.35 (s, 24H, Ph–Si(CH$_3$)$_2$), 1.64 (s, 6H, CH$_3$), 2.00 (s, 1H, OH), 7.52 (d, 8H, J = 8.5 Hz, ArH), 7.56 (d, 8H, J = 8.5 Hz, ArH), 7.57 (d, 2H, J = 1.5 Hz, ArH), 7.62 (t, 1H, J = 1.5 Hz, ArH), 7.65 (d, 4H, J = 1.5 Hz, ArH), 7.69 (t, 2H, J = 1.5 Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 0.67, 1.13, 1.16, 1.78, 31.37, 64.66, 81.20, 88.09, 88.65, 89.01, 90.83, 95.16, 123.33, 123.43, 123.56, 123.64, 124.14, 130.71, 132.96, 134.07, 134.48, 134.50, 135.86, 140.84.

NMTS2H. **NMTS2Hip** (1.1 g, 0.57 mmol) allowed to react with sodium hydride in the same manner as described above. The crude product was purified by silica-gel column separation with hexane/ dichloromethane (1/1) as an eluent to give **NMTS2H** (0.49 g, 0.27 mmol). Yield 47%. TLC (hexane/CH$_2$-Cl$_2$ = 1/1): R_f = 0.82. IR (NaCl; cm^{-1}): 3306 (≡C–H), 2968 (C–H), 2230 (C≡C), 1262 (Si–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.04 (s, 24H, Ph–Si–O–Si–O–Si(CH$_3$)$_2$), 0.07 (s, 24H, Ph–Si–O–Si(CH$_3$)$_2$), 0.09 (s, 36H, Si(CH$_3$)$_3$), 0.36 (s, 24H, Ph–Si(CH$_3$)$_2$), 3.15 (s, 1H, C≡C–H), 7.52 (d, 8 H, J = 8.2 Hz, ArH), 7.56 (d, 8H, J = 8.2 Hz, ArH), 7.62 (d, 2H, J = 1.5 Hz, ArH), 7.66 (d, 4H, J = 1.5 Hz, ArH), 7.67 (t, 1H, J = 1.5 Hz, ArH), 7.69 (t, 2H, J = 1.5 Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 0.69, 1.15, 1.18, 1.80, 90.86, 94.28, 123.38, 124.17, 130.72, 132.98, 134.10, 140.87. Anal. Calcd for (C$_{92}$H$_{134}$O$_{12}$Si$_{16}$): C, 58.7; H, 7.2. Found: C, 58.6; H, 6.9.

Polymerization

An appropriate amount of monomers (typically, 0.5–1.0 g) was placed in an Schlenk tube equipped with a three-way stopcock, a rubber septum and a Teflon®-coated magnetic stirring bar. The tube was placed under vacuum, followed by an nitrogen backflush. Freshly distilled solvent was transferred to the tube, and the monomers were dissolved with stirring. The determined amount of [Rh(C$_7$H$_8$)Cl]$_2$ and triethylamine dissolved in the solvent was added to the stirred monomers solution. The detailed polymerization conditions are tabulated in Table I and II. The reaction solution was poured into methanol or methanol/benzene (3/2 v/v) to yield polymer precipitate. The precipitate was washed with the precipitant and then dried in vacuo to give a yellow polymer.

Poly(TMS1H). IR (KBr; cm^{-1}): 2960 (νCH$_3$), 1250 (νSi–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.05 (s, 18H, Si(CH$_3$)$_3$), 5.96 (s, 1H, *cis* proton), 6.90 (br, 2H, ArH), 7.15 (br, 4H, ArH), 7.23 (br, 4H, ArH), 7.35 (br, 1H, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ −1.15, 89.61, 90.28, 123.91 (br), 131.15 (br), 133.01 (br), 138.92 (br), 140.37 (br). UV-vis (CHCl$_3$): λ_{max} = 454 nm. Anal. Calcd for (C$_{30}$H$_{30}$Si$_2$): C, 80.7; H, 6.8. Found: C, 80.2; H, 6.9.

Poly(TMS2H). IR (KBr; cm^{-1}): 2960 (νCH$_3$), 1252 (νSi–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 0.06 (br, 36H, Si(CH$_3$)$_3$), 5.8 (shoulder, *cis* proton), 5.7–8.0 (br, 25–26H, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ −1.28, 88–91 (br), 123.26 (br), 130.74 (br), 132.92 (br), 140.32 (br). UV-vis (CHCl$_3$): λ_{max} = 457 nm. Anal. Calcd for (C$_{68}$H$_{62}$Si$_4$): C, 82.4; H, 6.3. Found: C, 82.8; H, 6.6.

Poly(TMS3H). IR (KBr; cm^{-1}): 2964 (νCH$_3$), 1254 (νSi–C). ^{1}H NMR (CDCl$_3$, 200 MHz; ppm): δ 0.2 (br, 72H, Si(CH$_3$)$_3$), 5.7–8.0 (br, 54H, ArH). Anal. Calcd for (C$_{144}$H$_{126}$Si$_8$): C, 83.1; H, 6.1. Found: C, 83.2; H, 6.4.

Poly(PMDS1H). IR (KBr; cm^{-1}): 2964 (νCH$_3$), 1258 (νSi–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ −0.04 (s, 18H, Si(CH$_3$)$_3$), 0.10 (s, 12H, Si(CH$_3$)$_2$), 5.88 (s, 1H, *cis* proton), 6.80 (br, 2H, ArH), 7.0–7.6 (br, 9 H, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 0.74, 1.93, 89.12, 89.7, 124.08 (br), 130.88 (br), 132.57 (br), 138.2 (br), 139.81 (br). UV-vis (CHCl$_3$): λ_{max} = 476 nm. Anal. Calcd for (C$_{144}$H$_{126}$Si$_8$): C, 83.1; H, 6.1. Found: C, 83.2; H, 6.2.

Poly(PMDS2H). IR (KBr; cm^{-1}): 2968 (νCH$_3$), 1262 (νSi–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ −0.02 (br, 36 H, Si(CH$_3$)$_3$), 0.10 (s, 24H, Si(CH$_3$)$_2$), 6.1 (shoulder, *cis* proton), 5.7–8.0 (br, 25–26H, ArH). UV-vis (CHCl$_3$): λ_{max} = 489 nm. Anal. Calcd for (C$_{76}$H$_{86}$O$_4$Si$_8$): C, 70.9; H, 6.7. Found: C, 70.9; H, 6.7.

Poly(NMTS1H). IR (KBr; cm^{-1}): 2968 (νCH$_3$), 1262 (νSi–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ −0.04 (s, 18H, Si(CH$_3$)$_3$), 0.02 (s, 24H, Si(CH$_3$)2), 0.12 (s, 12H, Si(CH$_3$)$_2$), 5.83 (s, 1H, cis proton), 6.77 (br, 2H, ArH), 7.0–8.0 (br, 9H, ArH). UV-vis (CHCl$_3$): λ_{max} = 484 nm. Anal. Calcd for (C$_{42}$H$_{66}$O$_6$Si$_8$): C, 56.6; H, 7.5. Found: C, 56.6; H, 7.3.

Poly(NMTS2H). IR (KBr; cm^{-1}): 2968 (νCH$_3$), 1262 (νSi–C). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ −0.06–0.1 (br, 108H, SiCH$_3$), 5.9 (shoulder, cis proton), 5.6–8.0 (br, 25–26H, ArH). UV-vis (CHCl$_3$): λ_{max} = 495 nm. Anal. Calcd for (C$_{92}$H$_{134}$O$_{12}$Si$_{16}$): C, 58.7; H, 7.2. Found: C, 58.6; H, 6.9.

Measurements

IR spectra were measured with a Hitachi IR 270-30 spectrometer. NMR (^{1}H, ^{13}C) spectra were measured with a Varian Unity 500SW (500 MHz) or a Varian Gemini 200H (200 MHz) spectrometer. Average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) were evaluated by coupling of gel permeation chromatography and low angle laser light scattering (GPC-LALLS) at 40°C on THF eluent using Tosoh Liquid Chromatograph instruments with SD-8000, CCPD, C0-8010, LS-8000, RI-8011, and PP8010. The optical spectra were measured with a JASCO Ubest V-550DS UV-vis spectrometer. The wide angle X-Ray scattering measurements were performed using a Rigaku Geigerflex with a graphite-monochromatized Cu-K_α radiation which was supplied at 40 kV and 20 mA. The density was determined by floating method according to the litereture 11c.

Scanning force microscopy was performed with a Nanoscope III (Digital Instruments) operating in the tapping mode at a resonance frequency of 200–400 kHz and using Si probes with a spring constant of 20–100 N m^{-1} and with an apex radius below 10 nm. Measurements were done in air at room temperature. Samples for the SFM experiments were prepared by the spin casting of dilute chloroform solution (0.05–0.005 mg mL^{-1}). The spin coating was done at room temperature at 500 rpm on mica as substrates.

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