Polydendron: Polymerization of Dendritic Phenylacetylene Monomers

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Received November 18, 1996

Revised Manuscript Received February 18, 1997

Recently, dendrimers have attracted much attention as the macromolecules with precisely defined three-dimensional structure in organic and polymer chemistry.[1] In particular, stiff dendrimers are expected as ideal model systems for studying how physical properties depend on molecular size and architecture because the stiff dendrimers have shape persistency in comparison with flexible dendrimers.[2] The shapes of dendrimers should be significantly affected by the core group structures. Most of the synthesized dendrimers were spherical or globular, except for a few examples,[3,4] and usually showed a low viscosity, which was unfavorable for bulk materials with molding and film-forming ability. If we use a linear molecule for the core group instead of a small spot molecule, a cylindrical or rodlike macromolecule with uniform diameter will be yielded, preserving the advantage of dendrimers such as well-defined dendritic structure with many functional groups localized on the periphery of the dendrimer. For the extension of the convergent approach, the cylindrical or rodlike dendrimer should be synthesized by polymerization of a polymerizable group attached to the focal point of the monodendron, and some synthetic efforts including copolymerization were attempted by some research groups.[4] The polydendrons with a high molecular weight would also have other properties, such as membrane-forming ability, that lead to application for highly selective membranes, and the well-defined dendritic and cylindrical structure is expected to play an important role on the permselectivity.

Substituted polyacetylenes can be synthesized stereoselectively by an appropriate polymerization catalyst[5,6] and have attracted attention as one of the most interesting functional polymers with electrical conductivity,[7] nonlinear optical[8] and magnetic properties,[9] and gas-selective[10] or enantioselective[11] permeability as their membrane properties. Therefore, we selected poly(phenylacetylene) for the central core molecule and synthesized polydendrons by the polymerization of monodendrons with the phenyleneethynylene repeating unit.

The monodendrons[12] were synthesized as shown in Scheme 1 by repetition of the coupling reaction of 3,5-dibromo-1-(3-hydroxy-3-methylbutynyl)benzene with the phenylacetylene derivatives of an earlier generation and the elimination reaction of a terminal acetylene-protecting group according to a modified literature procedure,[2] where (3,5-di-*tert*-butylphenyl)acetylene (DB0H) or [4-(trimethylsilyl)phenyl]acetylene (TMS0H) was used as the starting peripheral group to afford adequate solvent solubility. The monodendrons were polymerized with a rhodium catalyst, $[Rh(C_7H_8)Cl]_2$, and the polymerization mixtures were purified by precipitating the chloroform solution into methanol or methanol/benzene (3/2) to yield the polydendrons[13] as yellow powders (Table 1). The rhodium catalyst has been reported to be effective for the polymerization of monosubstituted acetylenes and ineffective for disubstituted acetylenes.[6] The monodendrons were also polymerized with selective reaction of the terminal acetylene group of the focal point. 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 $\equiv$C−H bond) in the IR spectrum, δ 3.12 (s, 1H, $\equiv$C−H) in ^{1}H NMR, and δ 78.30 and 82.04 in ^{13}C NMR, completely disappeared, retaining those of the inner acetylene group, i.e., δ 89.61 and 90.28 in ^{13}C NMR.

The dendritic poly(DB1H) was soluble in common organic solvents, such as chloroform and tetrahydrofuran, but insoluble in aliphatic hydrocarbons and alcohols, while poly(DB0H) was insoluble in common organic solvents, corresponding with the literature.[14] This solubility change was consistent with the fact that solubilities of mono- and tridendrons were improved as the molecular size grew.[2b] The TMS series indicated a better solubility than the DB series and gave well soluble polydendrons with a high degree of polymerization ($\overline{DP} > 10^3$) under the polymerization conditions. $\bar{M}_w$ from the polystyrene standard was smaller than that from low-angle laser light scattering (LALLS). In particular, the polystyrene standard $\bar{M}_w$ of poly(TMS2H) was much smaller than the LALLS $\bar{M}_w$, which indicated that the dendritic structure retained a very compact molecular size in the solution, as was observed in the case of other dendrimers.[1]

In ^{1}H NMR of the polydendrons, the peak at δ 5.8−6.0 assignable to the cis proton of the poly(phenylacetylene) main chain supported the stereoselective cis-rich polymer structure.[15] The visible absorption maxima (λ_{max}) of the TMS series significantly increased due to the construction of the dendritic structure (i.e., poly(TMS0H) (401 nm) to poly(TMS1H) (454 nm)), while that of the DB series slightly increased (i.e., poly(DB0H) (463 nm) to poly(DB1H) (478 nm)). In the poly(phenylacetylene)s with a bulky substituent at the meta position, such as DB0H, the substitution effect on the visible absorption was explained as follows: The main-chain π-conjugation was extended in comparison with the simple poly(phenylacetylene), which shows no maxima in the visible range, by the reduction of orbital mixing or coplanarity between the main chain and substituent, which is a consequence of the restricted bond rotation between the main chain and the phenyl ring and/or crowded packing of the side chain.[9c] The recent computational studies of poly(phenylacetylene) derivatives indicated 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.[9e,16] Therefore, it was assumed that our polydendrons were also significantly twisted between the main chain and the dendritic side chain and the dendron planes were arranged along the main chain (see Figure 1). The X-ray and density data also supported this figure. The wide-angle X-ray scattering of the polymers showed a crystalline peak at $2\theta = 5.8°$ (poly(TMS0H)), 4.4° (poly(TMS1H)), and 3.2° (poly(TMS2H)), which might be correlated to the (100) reflection of the pseudohexagonal lattice of rodlike molecules.[15,17] The interplanar d spacing increased with increasing generation as 15.2 (poly(TMS0H)), 20.1 (poly-

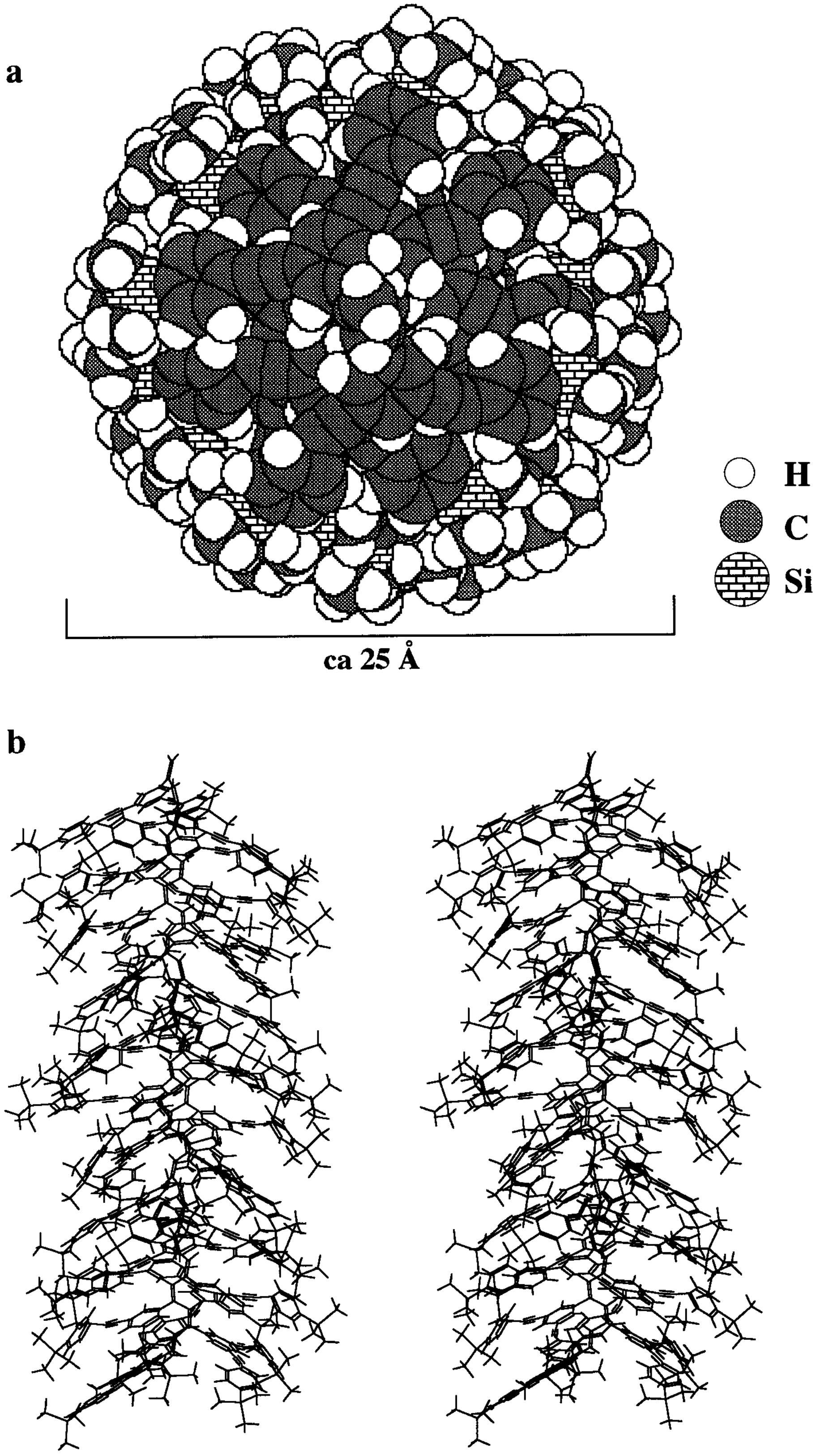

Figure 1. (a) Top view of space-filling models along the polymer chain. (b) Stereoview of the wire-frame model of poly(TMS1H) (24-mer).

(TMS1H)), and 27.6 (poly(TMS2H)) Å, respectively, while the density also increased as 0.962 ± 0.005 (poly(TMS0H)), 1.008 ± 0.005 (poly(TMS1H)), and 1.027 ± 0.006 (poly(TMS2H)) g/cm^3, respectively.[18] These experimental facts suggest that the increase of the *d* spacing is related to the increase of the column diameter with increasing generation. The column diameter estimated from the *d* spacing, 17.6 (poly(TMS0H)), 23.2 (poly(TMS1H)), and 31.9 (poly(TMS2H)) Å, almost agreed with molecular modeling (Figure 1). Some reasons why the monodendrons gave the polydendrons with high molecular weight in spite of their steric bulkiness were probably as follows. The terminal acetylene was exposed from the dendritic crowd, and

Scheme 1

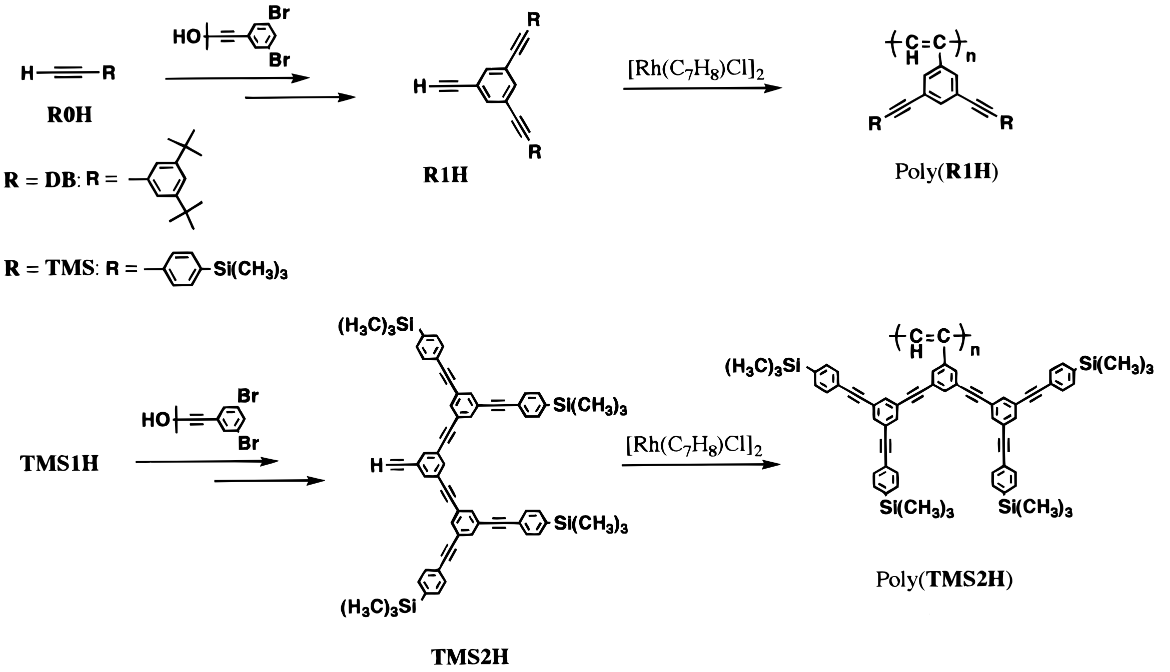

Table 1. Polymerization of Monomers[a] and Characterization of the Polymers

monomer	yield (%)	$\bar{M}_w$ ($\bar{M}_w/\bar{M}_n$)[b] (×10^6)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c] (×10^5)	$\overline{DP}$[d] (×10^3)	λ_{max}[e] (nm)	T_d[f] (°C)	membrane[g]
TMS2H	36[h]	2.8 (1.4)	3.4 (1.7)	2.8	457	368	+
TMS1H	83[h]	2.5 (1.4)	9.6 (1.4)	5.7	454	396	++
TMS0H	100[h]	1.3 (1.7)	2.7 (1.9)	7.6	401	304	++
DB1H	79[i]	0.56 (1.3)	1.1 (2.1)	1.1	478	298	−
DB0H	100[i]				463[j]	240[k]	−

[a] Polymerization conditions: chloroform (tetrahydrofuran for DB1H), $[M]_0$ = 0.2−0.5 M; $[Rh(C_7H_8)Cl]_2$−triethylamine (1:10), $[cat]_0/[M]_0$ = 1/20 to 1/2500; 25 °C; 2 h. [b] Measured by GPC-LALLS at 40 °C. [c] Measured by GPC calibrated with a polystyrene standard at 40 °C. [d] Calculated from $\bar{M}_w$ determined by GPC-LALLS. [e] Visible absorption maxima in chloroform. [f] Determined by thermogravimetric analysis in air. [g] Membrane forming ability: −, poor; +, good; ++, tough. [h] Methanol/benzene = 3/2 insoluble fraction. [i] Methanol insoluble fraction. [j] Cited from ref 14. [k] Cited from ref 19.

the polymerization proceeded stereoregularly to give the reasonable packing of the side-chain dendrons.

In the differential scanning calorimetry (DSC) of the polydendrons, no glass transition temperatures (T_g) were detected, similarly to previously reported zero generation poly(phenylacetylene)s.[10b,19] The decomposition temperatures (T_d) of poly(DB1H), poly(TMS1H) and poly(TMS2H) were higher than those of poly(DB0H) and poly(TMS0H), respectively, and rather close to those of poly(phenyleneethynylene) derivatives (ca. 400 °C).[20] In the TMS series, the polydendrons indicated good membrane-forming ability similar to poly(TMS0H),[10b] and the gas permeability of the membrane was examined. The oxygen permeability coefficient (P_{O_2}) and the oxygen separation factor ($\alpha = P_{O_2}/P_{N_2}$) of poly(TMS1H) were 72 barrers [1 barrer = 1 × 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}] and 3.78, respectively.[21] The α was higher than that of poly(TMS0H) (α = 2.70),[10b] and this result affords potential application for a highly selective membrane to the polydendrons of the TMS series. The well-defined dendritic and rodlike structure of the polydendrons may also be effective for other above mentioned (electrical conductive,[7] nonlinear optical,[8] and magnetic[9]) properties for substituted polyacetylenes.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research (No. 08651048) from the Ministry of Education, Science and Culture, Japan.

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(12) Selected data, TMS1H: yield from TMS0H 84%; mp 89 °C; IR (KBr, cm^{-1}) 3312 ($\nu_{\mathrm{H-C\equiv}}$), 2964 ($\nu_{\mathrm{CH_3}}$), 2212 ($\nu_{\mathrm{C\equiv C}}$), 1252 ($\nu_{\mathrm{Si-C}}$); ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 7.69 (t, 1H, 1.5 Hz, ArH), 7.62 (d, 2H, 1.5 Hz, ArH), 7.52$_2$ (d, 4H, 8.3 Hz, ArH), 7.51$_7$ (d, 4H, 8.3 Hz, ArH), 3.12 (s, 1H, $HC\equiv C$), 0.30 (s, 18H, Si(CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$, ppm) δ 141.60, 134.67, 134.51, 133.26, 130.73, 124.08, 122.93, 122.82, 90.82, 87.96, 82.04, 78.30, −1.25. Anal. Calcd for ($C_{30}H_{30}Si_2$): C, 80.7; H, 6.8. Found: C, 80.5; H, 7.1. TMS2H: yield from TMS1H 56%; mp 207 °C; IR (KBr, cm^{-1}) 3316 ($\nu_{\mathrm{H-C\equiv}}$), 2964, 2932, 2856 ($\nu_{\mathrm{CH_3}}$), 2216 ($\nu_{\mathrm{C\equiv C}}$), 1252 ($\nu_{\mathrm{Si-C}}$); ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 7.69 (t, 2H, 1.5 Hz, ArH), 7.67 (t, 1H, 1.5 Hz, ArH), 7.66 (d, 4H, 1.5 Hz, ArH), 7.63 (d, 2H, 1.5 Hz, ArH), 7.52 (s, 16H, ArH), 3.15 (s, 1H, $HC\equiv C$), 0.29 (s, 36H, Si(CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$, ppm) δ 141.60, 134.88, 134.74, 134.50, 134.08, 133.27, 130.73, 124.18, 123.70, 123.37, 123.06, 122.96, 90.86, 89.21, 88.52, 88.04, 81.82, 78.63, −1.25. Anal. Calcd for ($C_{68}H_{62}Si_4$): C, 82.4; H, 6.3. Found: C, 82.9; H, 6.5.

(13) Selected data, poly(TMS1H): IR (KBr, cm^{-1}) 2960 ($\nu_{\mathrm{CH_3}}$), 1250 ($\nu_{\mathrm{Si-C}}$); ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 7.35 (br, 1H, ArH), 7.23 (br, 4H, ArH), 7.15 (br, 4H, ArH), 6.90 (br, 2H, ArH), 5.96 (s, 1H, cis proton), 0.05 (s, 18H, Si(CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$, ppm) δ 140.37 (br), 138.92 (br), 133.01 (br), 131.15 (br), 123.91 (br), 90.28, 89.61, −1.15. 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 ($\nu_{\mathrm{CH_3}}$), 1252 ($\nu_{\mathrm{Si-C}}$); ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) δ 8.0−5.7 (br, 25−26H, ArH), 5.8 (shoulder, cis proton), 0.06 (br, 36H, Si(CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$, ppm) δ 140.32 (br), 132.92 (br), 130.74 (br), 123.26 (br), 88−91 (br), −1.28. Anal. Calcd for ($C_{68}H_{62}Si_4$): C, 82.4; H, 6.3. Found: C, 82.8; H, 6.6.

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MA9616975