5816 *Macromolecules* **1992**, *25*, 5816–5820

Polymerization of Silicon-Containing Diphenylacetylenes and High Gas Permeability of the Product Polymers[1]

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Received January 21, 1992; Revised Manuscript Received June 21, 1992

ABSTRACT: Poly(diphenylacetylene) is thermally very stable, but insoluble in any solvent, whereas polyacetylenes from unsymmetrically disubstituted acetylenes are generally soluble. Hence, the synthesis of soluble poly(diphenylacetylenes) was examined by introducing the trimethylsilyl group. 1-Phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene and 1-phenyl-2-[*m*-(trimethylsilyl)phenyl]acetylene polymerized with $TaCl_5$–cocatalyst systems to provide new polymers with over 70% yields having a weight-average molecular weight over 1×10^6. As cocatalysts, *n*-Bu_4Sn, Et_3SiH, and 9BBN were especially effective. The polymers were yellow solids with the alternating double bond structure $[-CPh{=}C(C_6H_4SiMe_3)-]_n$. They completely dissolved in toluene, $CHCl_3$, etc., and formed tough films by solution casting. The onset temperatures of weight loss in TGA in air were as high as ca. 400 °C. Their oxygen permeability coefficients were both high, ca. 1000 barrers.

Introduction

Various substituted polyacetylenes have recently been synthesized by groups 5 and 6 transition-metal catalysts.[2] Among these polymers, poly(diphenylacetylene) [poly(DPA)] is obtained in good yields with $TaCl_5$–cocatalyst systems, and exhibits the highest thermal stability among substituted polyacetylenes (the temperature at which its weight loss starts in air is ~500 °C).[3] This polymer, however, does not dissolve in any solvents. In general, polymers from symmetrically disubstituted acetylenes tend to be insoluble in solvents. For instance, poly(2-octyne) and poly(3-octyne) are soluble in common organic solvents, whereas poly(4-octyne) is not.[4] Hence, if a bulky substituent is introduced into one phenyl group of diphenylacetylene (DPA), a soluble polymer is anticipated to form.

Among many unique properties of substituted polyacetylenes, silicon-containing polyacetylenes are particularly likely to show high gas permeability.[5] As an extreme example, the permeability of poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] to oxygen is higher than that of any other existing polymer, and has recently been under intensive research.[6]

It is, therefore, expected that poly(DPA)s having a trimethylsilyl group on one phenyl group will be soluble in organic solvents, and will exhibit high thermal stability and high gas permeability. It is also of interest to examine the influence of the trimethylsilyl group on polymerization behavior. To clarify these points, the polymerization of 1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene (*p*-Me_3SiDPA) and 1-phenyl-2-[*m*-(trimethylsilyl)phenyl]acetylene (*m*-Me_3SiDPA) and properties of the produced polymers, especially gas permeability, have been investigated in the present paper.

Results and Discussion

Polymerization by Various Catalysts. Polymerization of *p*-Me_3SiDPA was studied by using groups 5 and 6 transition-metal catalysts which are active in the polymerization of various substituted acetylenes (Table I). Though *p*-Me_3SiDPA was consumed to some extent with $TaCl_5$ alone, no methanol-insoluble polymer was produced. Very importantly, polymers were obtained when organometallic cocatalysts that are effective to DPA were added in a 2-fold excess to $TaCl_5$. Especially, *n*-Bu_4Sn, Et_3SiH, and 9-borabicyclo[3.3.1]nonane (9BBN) achieved virtually quantitative monomer conversions, and polymers were obtained in over 70% yields. *n*-BuLi and sodium bis(2-methoxyethoxy)aluminum hydride (vitride) were less effective; i.e., the monomer did not react so much, and the polymer yields were lower. All these cocatalysts, which are reducing or alkylating agents, are considered to participate in the generation of metal carbenes and to modify the propagating species. As expected, the polymers produced were soluble in toluene and $CHCl_3$ unlike poly(DPA). Many of the weight-average molecular weights ($\bar{M}_w$) of polymers exceeded 2×10^6 according to gel permeation chromatography (GPC; polystyrene calibration).

Table I
Polymerization of *p*-Me_3SiDPA by Various Catalysts[a]

no.	catalyst	monomer convn, %	polymer[b] yield, %	polymer[b] $\bar{M}_w/10^3$ [c]	polymer[b] $\bar{M}_n/10^3$ [c]
1	$TaCl_5$	31	0		
2	$TaCl_5$–*n*-Bu_4Sn	95	85	2200	750
3	$TaCl_5$–Et_3SiH	100	71	2100	570
4	$TaCl_5$–9BBN[d]	100	91	2300	720
5	$TaCl_5$–*n*-BuLi	72	60	2100	530
6	$TaCl_5$–vitride[e]	31	25	1100	320
7	$NbCl_5$–*n*-Bu_4Sn	34	0		
8	WCl_6–*n*-Bu_4Sn	19	0		
9	$MoCl_5$–*n*-Bu_4Sn	18	0		

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 0.50 M, [cat.] = 20 mM, and [cocat.] = 40 mM. [b] Methanol-insoluble product. [c] Determined by GPC. [d] 9BBN = 9-borabicyclo[3.3.1]nonane. [e] Vitride = sodium bis(2-methoxyethoxy)aluminum hydride.

No polymer was obtained from *p*-Me_3SiDPA with $NbCl_5$–*n*-Bu_4Sn (see Table I), though this catalyst effects polymerization of disubstituted acetylenes like 1-phenyl-1-propyne and 1-(trimethylsilyl)-1-propyne. WCl_6–*n*-Bu_4Sn and $MoCl_5$–*n*-Bu_4Sn, which polymerize various monosubstituted and some disubstituted acetylenes,[2] gave no polymer, either. The result that only the $TaCl_5$–cocatalyst system is useful is also the case with DPA,[3] being associated with the remarkable steric effect of the monomers. The methanol-soluble products (differences between the monomer conversion and the polymer yield in Table I) were all linear oligomers according to GPC (several sequential peaks below molecular weight 2000).

The polymerization of *m*-Me_3SiDPA was examined using various catalysts (Table II). When $TaCl_5$ was employed in conjunction with suitable cocatalysts such as *n*-Bu_4Sn, Et_3SiH, and 9BBN, the yields of methanol-insoluble

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Table II
Polymerization of *m*-Me$_3$SiDPA by Various Catalysts[a]

no.	catalyst	monomer convn, %	polymer[b] yield, %	$\bar{M}_w/10^3$ [c]	$\bar{M}_n/10^3$ [c]
1	$TaCl_5$	21	0		
2	$TaCl_5$–*n*-Bu_4Sn	100	87	1400	250
3	$TaCl_5$–Et_3SiH	100	93	1000	210
4	$TaCl_5$–9BBN[d]	100	73	1300	280
5	$TaCl_5$–*n*-BuLi	66	44	970	180
6	$TaCl_5$–vitride[e]	43	31	460	32
7	$NbCl_5$–*n*-Bu_4Sn	25	0		
8	WCl_6–*n*-Bu_4Sn	10	0		
9	$MoCl_5$–*n*-Bu_4Sn	18	0		

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0 = 0.50$ M, [cat.] = 20 mM, and [cocat.] = 40 mM. [b] Methanol-insoluble product. [c] Determined by GPC. [d] 9BBN = 9-borabicyclo[3.3.1]nonane. [e] Vitride = sodium bis(2-methoxyethoxy)aluminum hydride.

Table III
Solvent Effects on the Polymerization of *p*-Me$_3$SiDPA and *m*-Me$_3$SiDPA by TaCl$_5$–*n*-Bu$_4$Sn (1:2)[a]

solvent	monomer convn, %	polymer[b] yield, %	$\bar{M}_w/10^3$ [c]	$\bar{M}_n/10^3$ [c]
		p-Me$_3$SiDPA		
toluene	95	85	2200	750
heptane	100	79	2100	810
PhCl	81	72	2000	680
$(CH_2Cl)_2$	81	68	1800	580
PhOMe	0	0		
		m-Me$_3$SiDPA		
toluene	100	87	1400	250
heptane	70	53	1300	210
PhCl	81	70	1100	230
$(CH_2Cl)_2$	75	52	910	150
PhOMe	0	0		

[a] Polymerized at 80 °C for 24 h; $[M]_0 = 0.50$ M, $[TaCl_5] = 20$ mM, and [*n*-Bu_4Sn] = 40 mM. [b] Methanol-insoluble product. [c] Determined by GPC.

polymers exceeded 70%. The M_w values of the polymers were 1×10^6 and above. *n*-BuLi and vitride were less effective as cocatalysts, as is judged from the polymer yields and molecular weights. Catalysts composed of $TaCl_5$ alone, $NbCl_5$–*n*-Bu_4Sn, WCl_6–*n*-Bu_4Sn, and $MoCl_5$–*n*-Bu_4Sn did not produce methanol-insoluble polymer. Thus, *m*-Me$_3$SiDPA behaves in polymerization similarly to *p*-Me$_3$SiDPA and DPA, although the molecular weight of poly(*m*-Me$_3$SiDPA) is somewhat lower than that of poly(*p*-Me$_3$SiDPA).

Polymerization with TaCl$_5$–*n*-Bu$_4$Sn. Effects of polymerization conditions were studied by using $TaCl_5$–*n*-Bu_4Sn which proved to be one of the most effective catalysts in the polymerization of *p*-Me$_3$SiDPA and *m*-Me$_3$SiDPA.

Solvent effects on the polymerization of *p*-Me$_3$SiDPA and *m*-Me$_3$SiDPA by $TaCl_5$–*n*-Bu_4Sn were studied (Table III). The polymerization of both monomers proceeded in heptane and chlorine-containing solvents [PhCl and $(CH_2Cl)_2$] as well as in toluene, and polymers were formed in good yields. The $\bar{M}_w$ values were not very different from those in toluene. On the other hand, no polymerization occurred in anisole, which is a useful solvent for the preparation of all-cis poly(*tert*-butylacetylene).[2b]

Figure 1 shows the effect of temperature on the polymerization of *p*-Me$_3$SiDPA and *m*-Me$_3$SiDPA. Polymers were obtained at 30 °C and above from both monomers. The polymer yields increased with increasing temperature, and leveled off at 80 °C and above. The molecular weights of polymers hardly changed in the temperature range examined, being ca. 2×10^6 with poly(*p*-Me$_3$SiDPA) and 1×10^6 with poly(*m*-Me$_3$SiDPA).

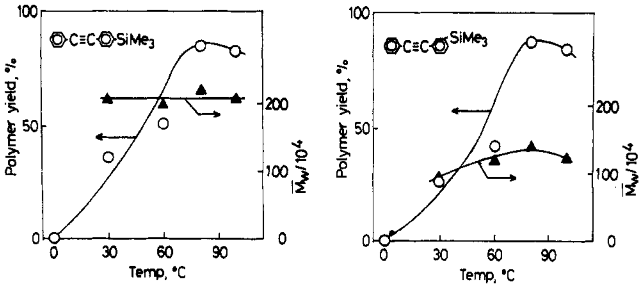


Figure 1. Effects of temperature on the polymerization of *p*-Me$_3$SiDPA and *m*-Me$_3$SiDPA by $TaCl_5$–*n*-Bu_4Sn (in toluene, 24 h, $[M]_0 = 0.50$ M, $[TaCl_5] = 20$ mM, [*n*-Bu_4Sn] = 40 mM).

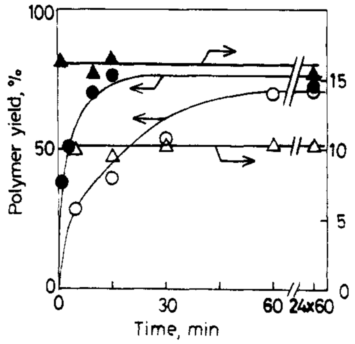


Figure 2. Time profiles of the polymerization of *p*-Me$_3$SiDPA and *m*-Me$_3$SiDPA by $TaCl_5$–*n*-Bu_4Sn (in toluene, 80 °C, $[M]_0 = 0.50$ M, $[TaCl_5] = 20$ mM, [*n*-Bu_4Sn] = 40 mM).

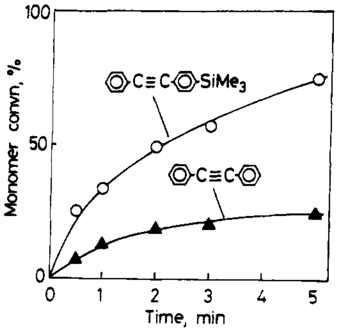


Figure 3. Copolymerization of *p*-Me$_3$SiDPA with DPA by $TaCl_5$–*n*-Bu_4Sn (in toluene, 80 °C, $[M_1]_0 = [M_2]_0 = 0.25$ M, $[TaCl_5] = 20$ mM, [*n*-Bu_4Sn] = 40 mM).

As seen in Figure 2, the polymerization of *p*-Me$_3$SiDPA was completed within 15 min, and that of *m*-Me$_3$SiDPA in 90 min. Thus, both polymerizations are fairly rapid. The fact that the polymerization of *m*-Me$_3$SiDPA is slower is probably due to the steric hindrance of the *m*-SiMe$_3$ group. No changes in polymer molecular weight were observed, even though the polymerization systems were left over 24 h. This is indicative of the absence of polymer degradation after completion of polymerization which is seen in the polymerization of 1-phenyl-1-propyne.[7]

To clarify the influence of the trimethylsilyl group on the monomer reactivity, copolymerization of *p*-Me$_3$SiDPA with DPA was attempted with $TaCl_5$–*n*-Bu_4Sn catalyst in toluene. As seen in Figure 3, *p*-Me$_3$SiDPA was consumed faster than DPA. In general, the relative monomer reactivity in the copolymerization of substituted acetylenes is governed by both steric and electronic effects of substituent; i.e., the monomer reactivity decreases with increasing bulkiness of the substituent and/or with decreasing electron-donating ability of the substituent. Since *p*-Me$_3$SiDPA should be similar in the steric effect to DPA, the observed difference in relative reactivity seems to originate from the electron-donating property of the trimethylsilyl group.

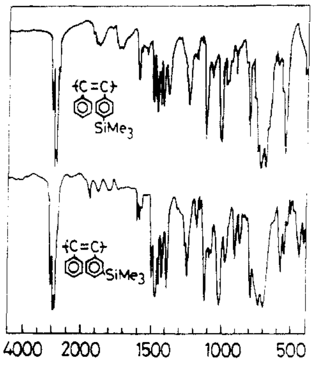


Figure 4. IR spectra of poly(p-Me$_3$SiDPA) and poly(m-Me$_3$SiDPA) (film; samples from Table I, no. 2, and Table II, no. 2).

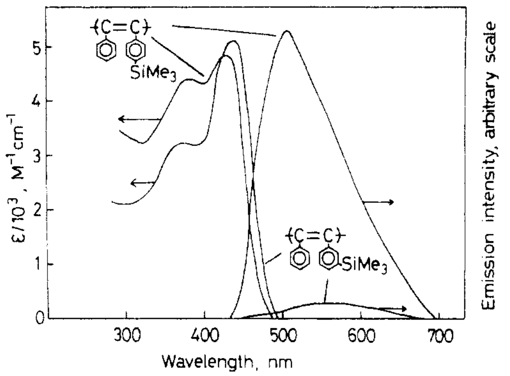


Figure 5. UV-visible and fluorescence spectra of poly(p-Me$_3$SiDPA) and poly(m-Me$_3$SiDPA) (measured in tetrahydrofuran; samples from Table I, no. 2, and Table II, no. 2).

Polymer Structure. The structure of poly(p-Me$_3$SiDPA) and poly(m-Me$_3$SiDPA) did not depend on the polymerization conditions. The data described below have been obtained with the polymer samples obtained with TaCl$_5$–n-Bu$_4$Sn in toluene (Table I, no. 2, and Table II, no. 2).

The elemental analysis data of poly(p-Me$_3$SiDPA) and poly(m-Me$_3$SiDPA) agreed well with their calculated values. Anal. Calcd for $(C_{17}H_{18}Si)_n$: C, 81.6; H, 7.2; Si, 11.2. Found for poly(p-Me$_3$SiDPA): C, 81.1; H, 8.0; Si, 10.9. Found for poly(m-Me$_3$SiDPA): C, 81.1; H, 7.7; Si, 11.2.

As seen from Figure 4, the IR spectra of poly(p-Me$_3$SiDPA) and poly(m-Me$_3$SiDPA) show no absorption due to C≡C stretching which was observed at 2100 cm^{-1} in the monomers. Strong absorptions characteristic of the SiC—H (1250 cm^{-1}) and Si—C (840 cm^{-1}) bonds are seen in both monomers and polymers.

In the ^{1}H NMR spectra of poly(p-Me$_3$SiDPA) and poly(m-Me$_3$SiDPA) broad signals due to the olefinic and aromatic protons (δ 7.5–5.5) and a sharp one due to the methyl protons (δ −0.2) were observed. No unassignable signals were seen. The ^{13}C NMR spectra of the polymers exhibited signals of sp^2 carbons (δ 150–125) and methyl carbons (δ 1), but showed no signals of sp carbons which were observed in both monomers around δ 90.

It is concluded that the present polymers possess alternating double bonds in the main chain. No information was, however, obtained regarding regiospecificity (head-to-tail and other structures) and geometric structure from IR and NMR spectra.

As seen in Figure 5, both polymers have two absorption maxima: poly(p-Me$_3$SiDPA) λ_{max} 375 nm (ϵ_{max} 4300 M^{-1}·cm^{-1}) and 430 nm (4800); poly(m-Me$_3$SiDPA) 380 nm (3200) and 440 nm (5100). The absorptions continue up to ca. 500 nm, which is in contrast to the absence of absorption in the visible region of the polymers from aliphatic disubstituted acetylenes.[2b] The present polymers fluoresced like poly(DPA), which is not the case with other types of polyacetylenes ever prepared. Since the present polymers were soluble, their emission spectra were measured in solution under excitation at 430 nm. The emission maxima were at 520 nm for poly(p-Me$_3$SiDPA) and at 550 nm for poly(m-Me$_3$SiDPA). The emission of the former polymer was about 10 times more intense for reasons which are not clear.

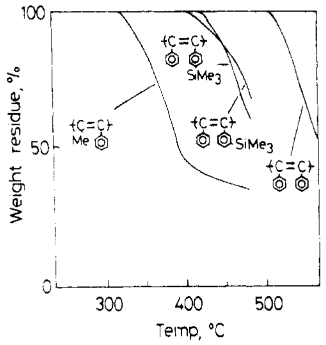


Figure 6. TGA curves of disubstituted acetylene polymers (in air, heating rate 10 °C/min; the present polymer samples from Table I, no. 2, and Table II, no. 2).

X-ray diffraction peaks obtained with Cu Kα radiation were as follows: poly(p-Me$_3$SiDPA) 2θ = 6.3° ($\Delta 2\theta/2\theta$ = 0.297), 14.3° (0.248); poly(m-Me$_3$SiDPA) 6.0° (0.280), 15.4° (0.461); poly(DPA) 8.6° (0.240), 16.3° (0.144), 22.6° (0.157). The ratio of the half-height width to the diffraction angle ($\Delta 2\theta/2\theta$) showed that the peaks were rather broad. Hence, it is concluded that all these polymers are amorphous. The insolubility of poly(DPA) should, eventually, be attributed to reasons other than crystallinity, such as a small surface area for interaction with solvent, of polymers from symmetrically disubstituted acetylenes.

Polymer Properties. Properties of the present polymers were hardly affected by polymerization conditions. Hence, properties were studied in detail using the same samples as employed for structural analysis.

Poly(p-Me$_3$SiDPA) and poly(m-Me$_3$SiDPA) were both yellow solids like poly(DPA). Poly(p-Me$_3$SiDPA) dissolved completely in benzene, toluene, cyclohexane, CCl$_4$, CHCl$_3$, tetrahydrofuran, anisole, diethyl ether, and triethylamine, whereas it partly dissolved in hexane, 1,4-dioxane, (CH$_2$Cl)$_2$, and ethyl acetate. Its nonsolvents include acetone, acetophenone, methyl benzoate, acetonitrile, N,N-dimethylformamide, and dimethyl sulfoxide. Though the solubility property of poly(m-Me$_3$SiDPA) was similar, it was totally soluble in hexane. Since poly(DPA) is insoluble in any of the above-stated solvents, introduction of a trimethylsilyl group is obviously effective in solubilizing poly(DPA). Free-standing films could be fabricated by casting the present polymers from toluene solution.

No weight loss of poly(DPA) occurs below 500 °C in TGA, demonstrating that it is more stable than any other substituted polyacetylenes.[3] The temperatures at which the weight loss of poly(p-Me$_3$SiDPA) and poly(m-Me$_3$SiDPA) started in air were 420 and 400 °C, respectively (Figure 6). These temperatures are lower than that of poly(DPA) but higher than those of most substituted polyacetylenes. Further, even when these polymers were left in air either at 120 °C for 20 h or at room temperature for 1 month, their molecular weights did not decrease. Thus, both of the present polymers possess high thermal stability.

Table IV
Gas Permeability of Silicon-Containing Polyacetylenes

	P^a						
polymer	He	H_2	O_2	N_2	CO_2	CH_4	P_{O_2}/P_{N_2}
poly(*p*-Me_3SiDPA)	1000	2100	1100	520	4700	1500	2.1
poly(*m*-Me_3SiDPA)	1000	2100	1200	610	4000	1500	2.0
poly(TMSP)	3300	7800	4500	2700	29 000	6500	1.7

[a] Gas permeability coefficients at 25 °C in the units of 1×10^{-10} cm^3(STP)·cm/(cm^2·s·cmHg) (=1 barrer).

Table V
Aging Effect on the Gas Permeability of Substituted Polyacetylenes

	before aging		after aging[a]	
polymer	P_{O_2}[b]	P_{O_2}/P_{N_2}	P_{O_2}[b]	P_{O_2}/P_{N_2}
poly(*p*-Me_3SiDPA)	1100	2.1	260	2.7
poly(*m*-Me_3SiDPA)	1200	2.0	67	2.9
poly(TMSP)	4500	1.7	56	3.1

[a] Aged at 80 °C for 26 h in vacuum; the values are the averages of a few measurements for each. [b] Oxygen permeability coefficients at 25 °C in the units of 1×10^{-10} cm^3(STP)·cm/(cm^2·s·cmHg).

The tensile properties of poly(*p*-Me_3SiDPA) and poly(*m*-Me_3SiDPA) measured at 25 °C are as follows:[8] Poly(*p*-Me_3SiDPA), Young's modulus $E = 1460$ MPa, tensile strength $\sigma_B = 19$ MPa, elongation at break $\gamma_B = 1.5\%$; poly(*m*-Me_3SiDPA), $E = 800$ MPa, $\sigma_B = 14$ MPa, $\gamma_B = 2.1\%$. Thus, both polymers are hard and brittle, and the position of the trimethylsilyl group does not greatly affect the tensile properties. The glass transition temperatures of the polymers were above 200 °C according to dynamic viscoelastic measurements.[8]

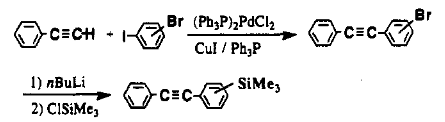
The electrical conductivity (25 °C) of poly(*m*-Me_3SiDPA) was 3×10^{-16} S·cm^{-1}, indicating that this polymer is a typical insulator like most substituted polyacetylenes.[2b]

Gas Permeability. The oxygen permeability coefficients (P_{O_2}) of poly(*p*-Me_3SiDPA) and poly(*m*-Me_3SiDPA) were ca. 1000 barrers [1 barrer = 1×10^{-10} cm^3(STP)·cm/(cm^2·s·cmHg)] (Table IV). These values correspond to about a quarter of that of poly(TMSP) which is the most gas-permeable existing polymer, and correspond to about twice that of poly(dimethylsiloxane) which is famous as the most gas-permeable rubbery polymer. Thus, the present polymers prove to be highly gas-permeable. Their separation factors between oxygen and nitrogen were about 2. No large differences between these polymers are seen in the permeabilities not only to oxygen but also to several other gases. Further, the permeabilities of the present polymers were $^1/_3$–$^1/_6$ the values of poly(TMSP) for all gases.

It is known that the gas permeability of poly(TMSP) decreases to ca. $^1/_{100}$ of its initial value if the polymer is kept in a vacuum for a long period of time.[9] Therefore, the effect of aging on the gas permeability of poly(*p*-Me_3SiDPA), poly(*m*-Me_3SiDPA), and poly(TMSP) was examined (Table V). The membranes were aged at 80 °C for 26 h in vacuum. Interestingly, the extent of the decrease of gas permeability varied depending on the kind of polymer. Thus, the P_{O_2} of poly(*p*-Me_3SiDPA) remained about a quarter of the original value, while that of poly(TMSP) decreased almost 100-fold. However, the values after aging are not very reproducible since they depend on various factors such as membrane thickness.

Experimental Section

Materials. The monomers (new compounds) were synthesized according to the following scheme with reference to the literature methods for ethynylation[10] and silylation.[11]



The procedure for preparing *p*-Me_3SiDPA is described below as an example.

1-(*p*-Bromophenyl)-2-phenylacetylene. A 1-L, round-bottom flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar, and was then flushed with dry nitrogen. Triethylamine (300 mL), $(Ph_3P)_2PdCl_2$ (0.56 g, 0.80 mmol), CuI (0.91 g, 4.8 mmol), Ph_3P (0.84 g, 3.2 mmol), and phenylacetylene (22.0 mL, 0.20 mol) were placed in the flask, and the mixture was stirred for 1 h. Then, *p*-bromoiodobenzene (56.6 g, 0.20 mol) in triethylamine (300 mL) was added dropwise, and stirring was continued for an additional 1 h. After the completion of the reaction had been confirmed by gas chromatography (GC), triethylamine was evaporated. Diethyl ether (ca. 400 mL) was added, and insoluble salts were removed by filtration. The solution was washed with 5% hydrochloric acid and water. The organic phase was dried over anhydrous sodium sulfate overnight, and diethyl ether was evaporated. The product was used for the next step without further purification: yield 55%, purity 99% (GC).

***p*-Me_3SiDPA.** A 200-mL, round-bottom flask was equipped with a three-way stopcock, a dropping funnel, and a magnetic stirring bar. After the flask was flushed with nitrogen, a hexane solution of *n*-butyllithium (63 mL, 1.6 M, 0.10 mol) was placed in the flask, and a part of the hexane (ca. 40 mL) was evaporated with an aspirator under magnetic stirring. Diethyl ether (40 mL; dried over sodium) was gradually added at −20 °C. At the same temperature, a solution of 1-(*p*-bromophenyl)-2-phenylacetylene (25.7 g, 0.10 mol) in diethyl ether (50 mL) was added dropwise, and the reaction mixture was left for 30 min. At −20 °C trimethylchlorosilane (13.9 mL, 0.11 mol) was added dropwise, and stirring continued for an additional 1 h at room temperature. After the completion of the reaction had been confirmed by GC, ice–water (20 mL) was added. The product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate overnight. Diethyl ether was evaporated, and the product was purified by flash column chromatography (Nakarai Tesque Co., silica gel 60; eluent, hexane): yield 70%, purity >99% (GC), d^{20} 1.051.

m-Me_3SiDPA was prepared in the same way from *m*-bromoiodobenzene: overall yield 30%, purity >99% (GC), d^{20} 1.022.

Transition-metal catalysts and organometallic cocatalysts were all commercially obtained, and used without purification, with care being taken not to allow decomposition by moisture and/or air. Polymerization solvents were purified by standard methods.

Polymerization. A typical procedure for the polymerization of *p*-Me_3SiDPA (cf. Table I, no. 2) is described below. The manipulation and reaction were carried out under dry nitrogen.

A monomer solution (2.4 mL) was prepared in a Schlenk tube by mixing *p*-Me_3SiDPA (0.71 mL, 0.75 g, 3.0 mmol), eicosane (0.50 mL; internal standard of GC), and toluene (1.19 mL). Another Schlenk tube was charged with $TaCl_5$ (35.8 mg, 0.10 mmol), *n*-Bu_4Sn (65.6 μL, 69.4 mg, 0.20 mmol), and toluene (3.0 mL); this catalyst solution was aged at 80 °C for 15 min. Then 2.0 mL of monomer solution was added to the catalyst solution. Polymerization was carried out at 80 °C for 24 h, which was quenched with a mixture of toluene and methanol (1 mL, volume ratio 4:1). After monomer conversion had been determined by GC (Silicon DC 550, 0.5 m, 180 °C), the polymerization mixture was diluted with toluene (300 mL) and was poured into methanol (4 L) under stirring to precipitate the formed polymer. The polymer was isolated by filtration and dried. The polymer yield was determined by gravimetry.

Characterization. The molecular weights of polymers were determined by gel permeation chromatography (GPC) with use of a polystyrene calibration. GPC curves were observed with a Shimadzu LC-9A liquid chromatograph [eluent, $CHCl_3$; columns, Shodex A805, A806, and A807 polystyrene gels (Showa Denko, Co., Japan)]. Monodisperse polystyrene samples with $\bar{M}_n$'s of

1.0×10^5, 3.0×10^5, 6.5×10^5, 1.8×10^6, 2.0×10^6, 3.8×10^6, and 2.0×10^7 were used to make a calibration curve.

NMR spectra were measured on a JEOL GSX-270 spectrometer. IR and UV–visible spectra were recorded with Shimadzu FTIR8100 and Shimadzu UV190 spectrophotometers, respectively. TGA was conducted with a Shimadzu 20B thermal analyzer (in air, heating rate 10 °C/min). The gas permeation was observed on a K-315-N gas permeability apparatus (Rikaseiki Co., Japan) by using solvent-cast membranes with a thickness of about 30 μm.

Acknowledgment. We thank Dr. K. Tamao (Department of Synthetic Chemistry, Kyoto University) for helpful discussion about monomer synthesis, and Dr. T. Hashimoto and Mr. K. Saijo (Department of Polymer Chemistry, Kyoto University) for the measurement of X-ray diffraction. Thanks are also due to Mr. M. Otsubo and Dr. Y. Hirokawa (Research and Development Center, Nippon Zeon Co., Ltd.) for examination of the aging effect on gas permeability. This research was partly supported by a Grant-in-Aid "New Functionality Materials" from the Ministry of Education, Science, and Culture, Japan (No. 02205068).

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Registry No. *p*-Me_3SiDPA, 136459-72-8; *p*-Me_3SiDPA (homopolymer), 136459-73-9; *m*-Me_3SiDPA, 136459-74-0; *m*-Me_3SiDPA (homopolymer), 136459-75-1; $TaCl_5$, 7721-01-9; *n*-Bu_4Sn, 1461-25-2; Et_3SiH, 617-86-7; 9BBN, 280-64-8; *n*-BuLi, 109-72-8; PhCl, 108-90-7; $(CH_2Cl)_2$, 107-06-2; PhMe, 108-88-3; $H(CH_2)_7H$, 142-82-5; He, 7440-59-7; H_2, 1333-74-0; O_2, 7782-44-7; N_2, 7727-37-9; CO_2, 124-38-9; CH_4, 74-82-8; $PhC{\equiv}CH$, 536-74-3; IC_6H_4-*p*-Br, 589-87-7; $PhC{\equiv}CC_6H_4$-*p*-Br, 13667-12-4; Me_3SiCl, 75-77-4; IC_6H_4-*m*-Br, 591-18-4; vitride, 22722-98-1.