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Synthesis and Properties of Indan-Based Polyacetylenes That Feature the Highest Gas Permeability among All the Existing Polymers

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ABSTRACT: Acetylenic monomers containing indan and other groups (**1a−m**) were polymerized with $TaCl_5$-*n*-Bu_4Sn catalyst to give high molecular weight polymers. Most polymers were soluble in common organic solvents including toluene and chloroform, and they afforded free-standing membranes by the solution casting method. The onset temperature of weight loss of the polymers were over 400 °C, indicating high thermal stability. Despite the absence of bulky spherical groups, polymethylated indan-containing polymer membranes showed extremely high gas permeability. In particular, the oxygen permeability coefficients of polymers having 1,1,3,3-tetramethylindan and either *p*-fluorophenyl or *p*,*m*-difluorophenyl groups (**2b** and **2e**) reached 17 900 and 18 700 barrers, respectively, which are even larger than that of the most permeable polymer known, poly(1-trimethylsilyl-1-propyne).

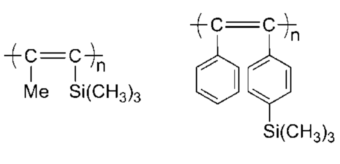
Introduction

The design and synthesis of substituted polyacetylenes are motivated by the development of new materials that display interesting physical and chemical properties. They find potential applications in optoelectronics, stimuli-responsive materials, gas separation membranes, and other fields.[1] Substituted polyacetylenes are an important category of separation membrane materials characterized by high gas permeability and high vapor/gas selectivity, and they exhibit strikingly different properties from those of conventional glassy polymers.[2] The unique permeation properties of these polymers are mainly attributed to their large excess free volume, which originates from their stiff main chain, bulky substituents, and low cohesive energy structure.[2,3]

Attracting the most attention within this family of materials is poly(1-trimethylsilyl-1-propyne) (PTMSP; Chart 1), which displays the highest gas permeability among all known polymers; many studies concerning the permeation properties of this polymer have been reported to date.[2d,4] Since the discovery of PTMSP, various substituted polyacetylenes have been synthesized in efforts to develop even more gas-permeable polymers. Poly(diphenylacetylenes) with bulky spherical substituents [e.g., poly[1-phenyl-2-(*p*-trimethylsilylphenyl)acetylene] (PTMSDPA) and its derivatives] are another important group of substituted polyacetylenes which show excellent thermal stability and high gas permeability.[5] Although the incorporation of bulky spherical groups such as trimethylsilyl and trifluoromethyl groups leading to sterically demanding structures has been recognized to favor high gas permeability, polymers more permeable than PTMSP have not been found yet.

We have recently developed a new class of polyacetylenes, namely polymethylated indan-containing poly(diphenylacetylene) derivatives, which show high gas permeability despite the absence of bulky spherical groups. In particular, the oxygen permeability of poly[1-(1,1,3,3-tetramethylindan-5-yl)-2-phenylacetylene] (Scheme 1; **2a**) is practically the same as that of PTMSP. This work has been published as a communication.[6] On the other hand, it has been reported that the incorporation of halogen atoms enhances the fractional free volume and, in turn, gas permeability of polymer membranes.[5d,7] By combining these two previous results, there is a possibility that we can develop a novel polymer material showing higher gas permeability than any existing polymers.

Chart 1. Structures of PTMSP and PTMSDPA



PTMSP PTMSDPA

In the present study, the polymerization of various diphenylacetylene monomers containing tetramethylindan (**1a−j**) was examined, and general properties of the formed polymers were elucidated. Furthermore, free-standing membranes were fabricated from most of the polymers (**2a−c** and **2e−i**), and their gas permeability was examined. Analogous poly(diphenylacetylenes) having either a hexamethylindan or indan group (**2k−m**) are also discussed for comparison.

Results and Discussion

Polymerization of Monomers. The polymerization of monomers **1a−m** was examined by using $TaCl_5$-*n*-Bu_4Sn catalyst (Table 1). It has been reported that $TaCl_5$-*n*-Bu_4Sn satisfactorily polymerizes sterically crowded disubstituted acetylenes including diphenylacetylene derivatives to give polymers with high molecular weights,[1a,b] which is essential for fabrication of free-standing membranes. In the present study, monomer **1a** afforded a polymer with a high weight-average molecular weight (M_w = 1.0×10^6) in a high yield (65%). Fluorine-containing monomers **1b−f** except **1d** also gave high molecular weight polymers with M_w's ranging from 9.2×10^5 to 2.9×10^6 in high yields (≥66%). Less polymerizability of monomer **1d** is attributable to the steric effect of the *o*-fluorine atom. Monomers **1g−i** having chlorine, bromine, and methyl groups, respectively, produced polymers with high molecular weights as well, whereas monomer **1j**, which has a bulkier trimethylsilyl group,

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Scheme 1. Synthesis of Indan-Containing Poly(diphenylacetylene) Derivatives

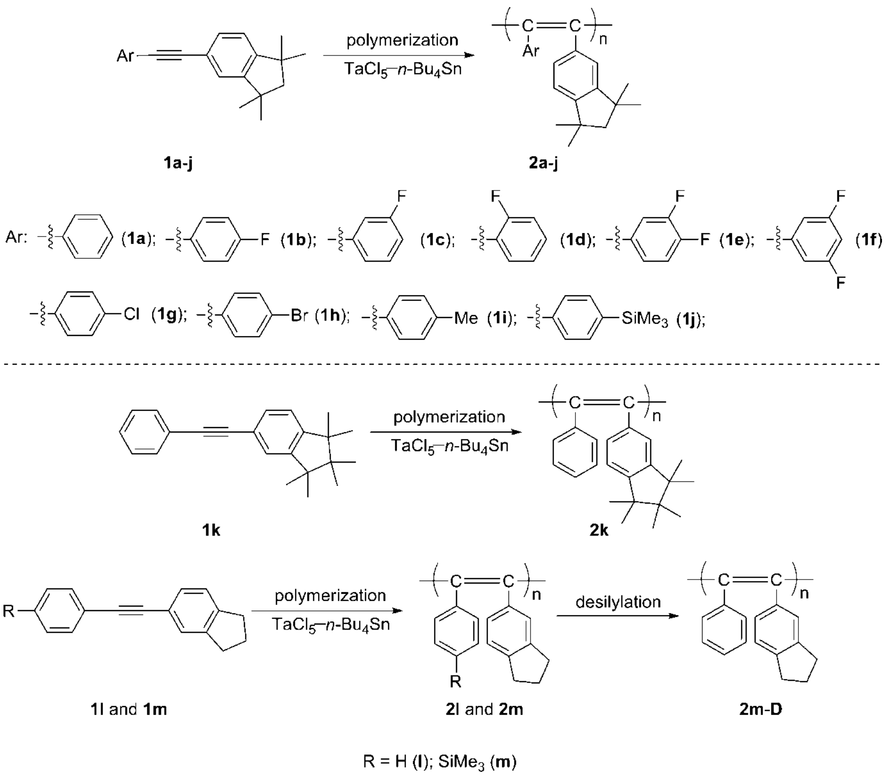


Table 1. Polymerization of Monomers 1a−m with $TaCl_5$-*n*-Bu_4Sn[a]

monomer	polymer[b] yield (%)	$M_w \times 10^{-3}$ [c]	M_w/M_n [c]
1a	65	1000	3.9
1b	74	1200	4.0
1c	66	920	3.5
1d	21	220	6.9
1e	67	1100	2.2
1f	73	2900	6.7
1g	41	700	9.9
1h	63	1100	3.5
1i	40	820	8.1
1j	15	150	4.0
1k	67	1500	3.3
1l	65[d]	–[e]	–[e]
1m	50[d]	2 000	3.8

[a] Polymerization in cyclohexane at 80 °C for 24 h; $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM. [b] Methanol-insoluble product. [c] Determined by GPC eluted with $CHCl_3$ (polystyrenes as standards). [d] Polymerization in toluene. [e] Insoluble in any solvents.

gave a polymer with a relatively low molecular weight ($M_w = 1.5 \times 10^5$) in a low yield (15%). Both hexamethylindan- and indan-based monomers **1k** and **1l** also polymerized in good yields. However, the indan-based polymer **2l** was insoluble in any organic solvents. It has been reported that poly(diphenylacetylene) is insoluble, while its *p*-trimethylsilyl derivatives, PTMSDPA is soluble.[5g,h] Similarly, trimethylsilyl-containing indan-based polymer **2m** was soluble.

General Properties of the Polymers. Polymer **2a** exhibited no IR absorption at 2215 cm^{-1} assignable to the triple bond of monomer **1a**, indicating both complete conversion of the triple bond of the monomer during polymerization and no contamination with the monomer in the polymeric product (Figure 1). This was the case with all polymers considered in the present study.

Figure 2 depicts the UV−vis spectra of **2a**, **2b**, and **2k**. The present polymers showed two characteristic UV−vis absorption maxima around 375 and 430 nm, which are due to the π-π^* transition of the conjugated system. The cutoff wavelength is approximately 500 nm. Similar spectra were observed in the cases also with other polymers in the present study.

Solubility properties of the obtained polymers are summarized in Table 2. Polymethylated indan- or trimethylsilyl-containing polymers **2a**−**k** and **2m** are readily soluble in common organic solvents including toluene, $CHCl_3$, and THF. In contrast, polymer **2l** having just planar indan and phenyl groups did not dissolve in any organic solvents examined. These results indicate that incorporation of polymethylated groups or trimethylsilyl groups is effective to enhance the solubility of the present polymers.

The thermal stability of the polymers was examined by TGA in air (Figures 3 and 4). The onset temperatures of weight loss of polymers **2a**−**m** were all approximately 410 °C and obviously higher than that of PTMSP (300 °C),[4e] indicating excellent thermal stability of the present polymers. The weight residue of Si-containing polymer **2m** did not become zero at high

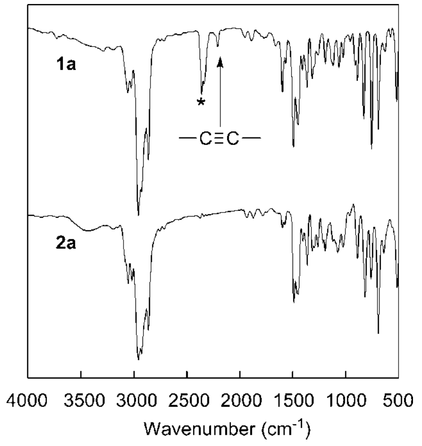


Figure 1. IR spectra of monomer **1a** and polymer **2a** (*: CO_2).

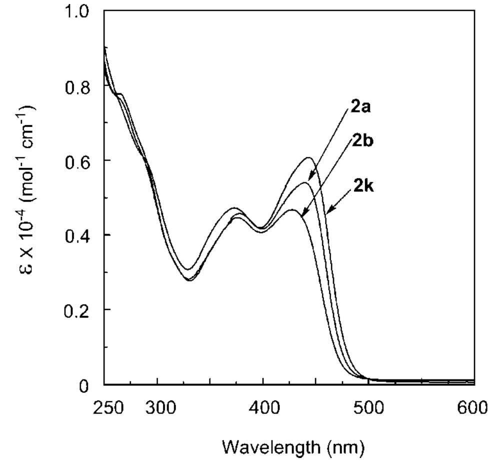


Figure 2. UV−vis spectra of polymers **2a**, **2b**, and **2k** measured in $CHCl_3$ ($c = 0.331-0.364$ mM).

Table 2. Solubility of the Polymers[a]

	2a	2b−h	2i−k	2l	2m	2m-D
hexane	±	−	±	−	+	−
cyclohexane	+	±	+	−	+	−
toluene	+	+	+	−	+	−
$CHCl_3$	+	+	+	−	+	−
THF	+	+	+	−	+	−
methanol	−	−	−	−	−	−
DMF	−	−	−	−	−	−
DMSO	−	−	−	−	−	−

[a] Symbols: (+) soluble; (±) partly soluble; (−) insoluble.

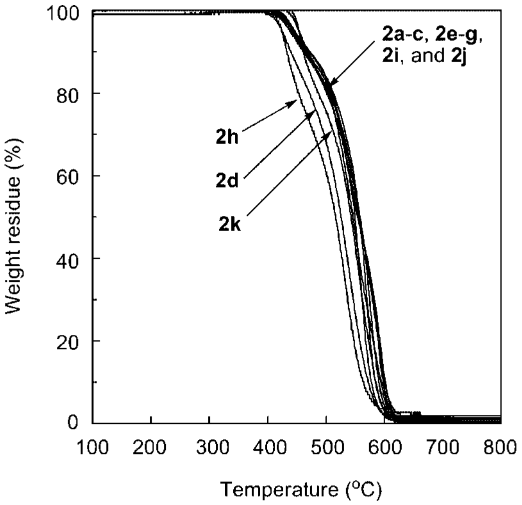


Figure 3. TGA curves of tetramethylindan-containing poly(diphenylacetylene)s **2a**−**k** (in air, heating rate 10 °C/min).

temperature unlike other polymers, which is explained by the formation of SiO_2.

Fabrication and Desilylation of Membranes. Free-standing membranes could be fabricated by casting polymers **2a**−**c**, **2e**−**i**, **2k**, and **2m** from toluene solution, whereas the membranes of **2d**, **2j**, and **2l** could not be prepared due to their low molecular weight or insolubility. Desilylation of Si-containing poly(diarylacetylene) membranes can provide solvent-insoluble membranes that cannot be prepared by solution casting.[5c−e] A membrane of polymer **2m-D** which has the same structure as that of **2l** was obtained by desilylation of **2m**. The desilylation reaction was performed in a trifluoroacetic acid/H_2O mixture (9:1 volume ratio) at room temperature for 24 h. The completion of desilylation can be confirmed by the fact that no SiO_2 remains at high temperature in the TGA analysis of **2m-D** in air (Figure 4).

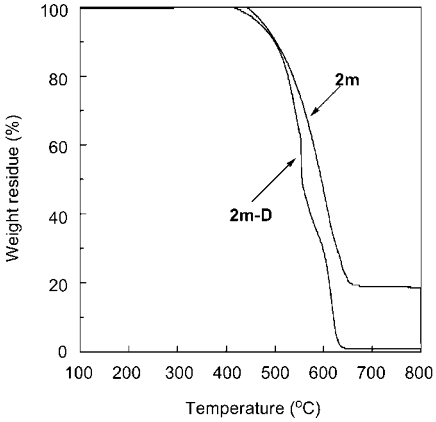


Figure 4. TGA curves of indan-containing poly(diphenylacetylene)s **2m** and **2m-D** (in air, heating rate 10 °C/min).

Table 3. Gas Permeability Coefficients (*P*) of Polymer Membranes[a]

polymer	substituent[b] on phenyl	*P* (barrer) He	H_2	O_2	N_2	CO_2	CH_4	PO_2/PN_2
2a	none	11 200	24 800	14 400	11 600	38 700	29 100	1.24
2b	*p*-F	15 800	33 300	17 900	15 600	47 000	34 300	1.15
2c	*m*-F	12 800	27 000	14 300	12 000	35 200	27 800	
2e	*p*,*m*-F_2	17 800	36 800	18 700	16 600	44 200	35 000	1.13
2f	*m*,*m*-F_2	13 700	28 500	15 200	13 100	36 100	29 100	1.16
2g	*p*-Cl	9300	20 600	11 700	9200	35 200	22 700	1.27
2h	*p*-Br	9200	20 700	11 400	9200	32 800	22 400	1.24
2i	*p*-Me	5000	10 800	5700	4100	16 900	10 100	1.39
2k	none	10 500	24 100	12 900	10 400	36 400	25 200	1.24
2m	*p*-$SiMe_3$	530	1100	450	170	2000	470	2.65
2m-D	none	200	360	86	30	390	60	2.87
PTMSP	none	9700	24 800	14 800	11 500	47 000	29 900	1.29

[a] Gas permeability coefficients at 25 °C in the units of 1×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) (= 1 barrer) (the values are average values of the two independent observed values using two different membranes; see Supporting Information for the original values). [b] The substituent on the phenyl group.

Gas Permeability of the Polymer Membranes. The gas permeability coefficients of the membranes are recorded in Table 3. All of polymethylated indan-containing polymers **2a-k** showed high gas permeability. Among them, the oxygen permeability coefficient (PO_2) of **2a** reached 14 400 barrers, which is about the same as that of PTMSP. In general, gases dissolve well in fluorinated compounds.[8] Therefore, the present polymers containing fluorine atom(s) are expected to show even higher gas permeability. In fact, polymers **2b** and **2e** which possess fluorine atoms at the *para* and *para*,*meta* positions of the phenyl ring, respectively, exhibited extremely high gas permeability, and their PO_2 values reached 17 900 and 18 700 barrers, respectively. These values are obviously larger than that of the most permeable PTMSP measured under the same conditions. Typical PO_2 values of PTMSP and PTMSDPA are around 10 000 and 1 500 barrers, respectively,[2a,b] which depend on the method of membrane preparation, measuring conditions, and storage time and conditions. Taking account of this, we measured the PO_2 of PTMSP under identical conditions with respect to both membrane fabrication and gas permeability measurement and obtain a value of 14 800 barrers as an average for two different pieces of membrane. Thus, we conclude that polymers **2b** and **2e** are more permeable to oxygen than PTMSP which has been known to the most gas-permeable among all existing polymers.

The following points are worth noting as features of tetramethylindan-based F-containing polymers: (i) the structure of **2b** and **2e** is quite different from that of PTMSP; (ii) a plural number of methyl groups of the indan moieties in **2b** and **2e** as well as in other polymers considered in this study generate high

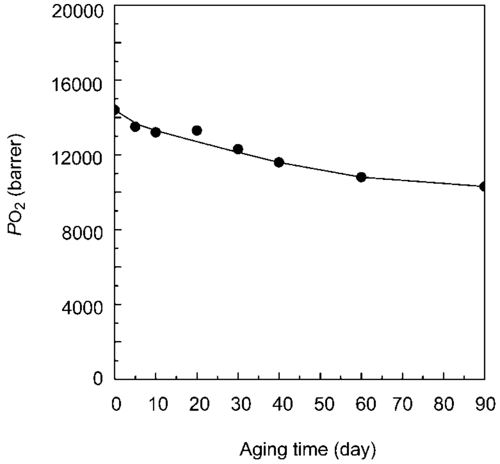


Figure 5. Effect of aging time on the oxygen permeability of polymer **2a** (stored in air at room temperature).

levels of excess free volumes and exhibit large local mobility through their rotation, thus facilitating the diffusion of gases;[9] (iii) polymer chain packing of **2b** and **2e** is inhibited by intermolecular repulsive force between fluorine atoms that have high electron density, producing more sparse structures in the polymer matrix; and (iv) membranes **2c** and **2f** containing fluorine at the *meta* and *meta*,*meta*-positions of the phenyl ring displayed somewhat lower PO_2 values (14 300 and 15 200 barrers, respectively) than their counterparts with fluorine atoms at *para* positions **2b** and **2e**, indicating that incorporation of fluorine atoms at the *para* position is more effective to enhance gas permeability among the polymers considered in this study.

Effects of various substituents (R's) in the phenyl ring of tetramethylindan-based polymers on gas permeability were examined to see how the electron density and steric bulkiness affect gas permeability. It turned out that the group R displays large effects on gas permeability. Gas permeability decreased with increasing bulkiness of the ring substituent R [ν_w (van der Waals radii) = 5.7 (F), 12.0 (Cl), 13.7 (Me), 14.4 (Br) cm^3/mol].[10] For instance, the PO_2 values of **2g** (R = Cl) and **2h** (R = Br) were 11 700 and 11 400, respectively, which are lower than that of **2b** (R = F). The lowest permeability in this series was observed in **2i** (R = Me) within this series, whose PO_2 value is about 1/3 that of **2b**. Although bromine and methyl groups are comparable in steric bulkiness, the PO_2 value of **2i** is about a half of that of **2h**, which indicates that the gas permeability of the present polymers depends not only on the bulkiness of the substituents but also on their electronegativity.

Hexamethylindan-based polymer **2k** also exhibited high oxygen permeability, reaching 12 500 barrers. In contrast, indan-based polymer **2m** and its desilylated counterpart **2m-D** showed much lower gas permeability (PO_2 = 450 and 86 barrers, respectively) than those of polymethylated indan-based polymers. This result implies that the methyl groups in the indan moiety play an important role in attaining high gas permeability. The PO_2/PN_2 ratios of these polymers are in a range of 1.13−2.87, and a clear tradeoff relationship is observed between permeability and permselectivity in accordance with a general tendency.[11]

The dependence of oxygen permeability of polymer **2a** (thickness: 85 μm) on aging time was examined (Figure 5), because it is known that the PO_2 value of PTMSP decreases with time.[12] The membrane was kept in a polyethylene sack at room temperature. The PO_2 value decreased from 14 400 to 12 300 barrers after 30 days and then to 10 800 barrers after 60 days, and then almost practically leveled off to 10 300 after 90 days. Thus, the PO_2 value of the present polymer decreased only to two thirds that of its initial value after 90 days. As a consequence, it can be said that the time dependence of PO_2 in this polymer is relatively small.

Membrane separation technology has recently emerged as a potential technique to remove higher hydrocarbons from natural gas.[13] Table 4 compares the permeability and permselectivity of **2a** and **2b** for pure and mixed gases of n-C_4H_{10} and CH_4. The n-C_4H_{10} permeability and permselectivity over CH_4 in mixed gas measurements are both higher than those estimated from pure gas data. For example, the n-C_4H_{10} permeability of **2a** in the mixed gas was 4 times higher than the pure gas permeability coefficient. In contrast, the CH_4 permeability decreased from 23 100 barrers in pure gas to 14 700 barrers in the mixed gas. As a consequence, the mixed gas permselectivity was 6 times that of the pure gas permselectivity. A similar tendency has been observed in PTMSP.[4a,20] The pure gas permeability studies were performed at a total feed pressure of n-C_4H_{10} of 1.4 atm, and the mixed gas permeability coefficients were determined at the same total feed pressure (i.e., 1.4 atm), but the n-C_4H_{10} content of the mixed gas feed was only 2%, which results in an n-C_4H_{10} feed partial pressure of 0.028 atm in the mixed gas case. In many glassy polymers, including substituted polyacetylenes, permeability of higher hydrocarbons increases significantly as feed partial pressure is lowered, due to so-called dual mode permeability effects.[20,21] This phenomenon explains the increase in the n-C_4H_{10} permeability. The reduction in CH_4 permeability is ascribed in part to competitive sorption effects, where the presence of highly condensable and strongly sorbing n-C_4H_{10} in the gas mixture effectively inhibits CH_4 from sorbing into the nonequillibrium excess volume sites in the polymer, thereby lowering the CH_4 solubility (and, in turn, permeability) due to the presence of n-C_4H_{10} in the polymer. Such competitive sorption effects have been observed in other substituted polyacetylenes[22] and have been shown to contribute directly to decreased permeability of the more weakly sorbed component (CH_4 in this case) and higher mixed gas selectivity. Additionally, it has been observed in other substituted polyacetylenes that the sorption of n-C_4H_{10} into the nonequilibrium excess free volume of the polymer actually lowers the overall free volume of the polymer/penetrant mixture, which acts to reduce the CH_4 diffusion coefficient through the polymer in the presence of n-C_4H_{10}.[20] This effect would also contribute toward lower CH_4 permeability in the presence of n-C_4H_{10}.

Conclusions

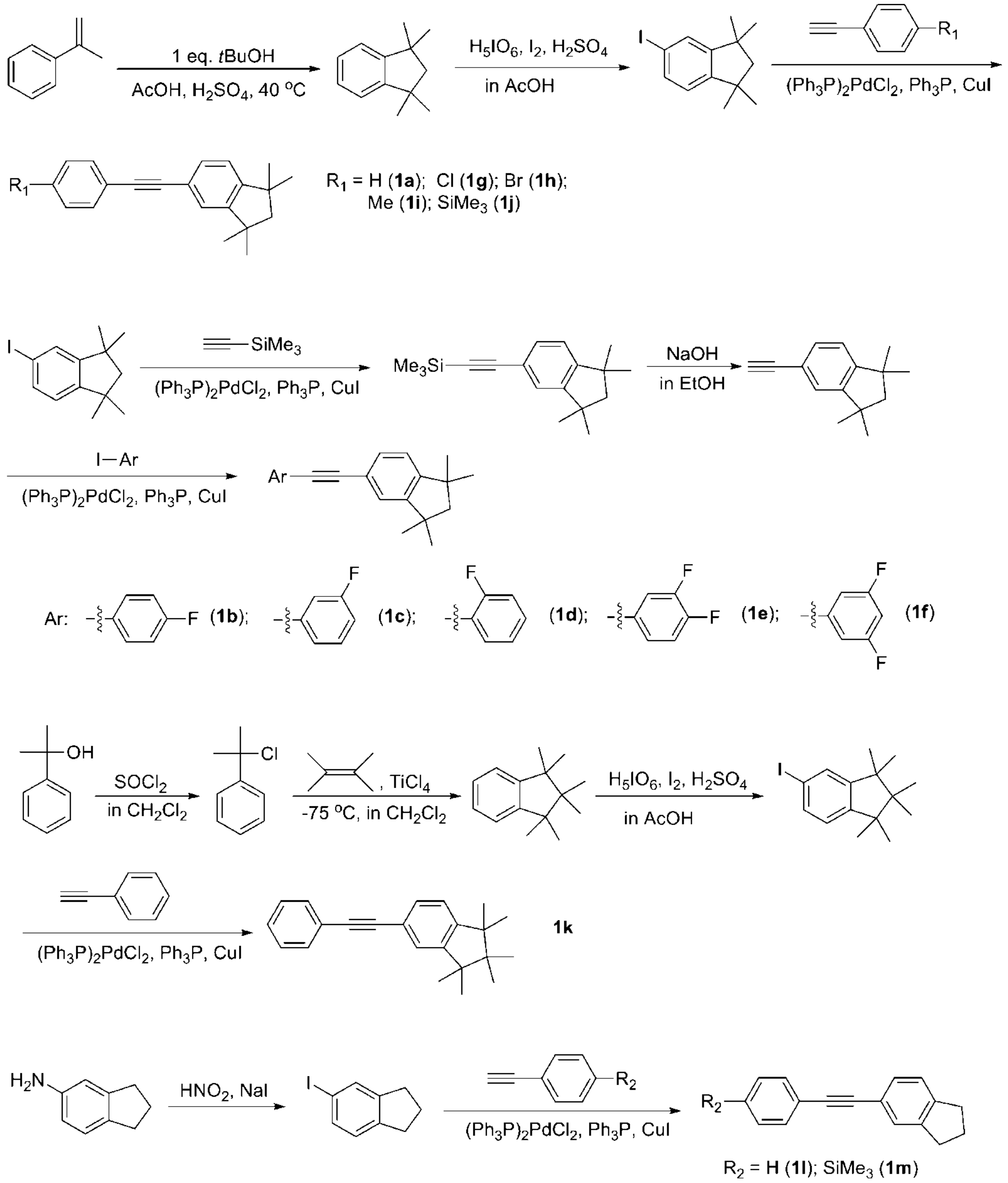
A series of novel polymethylated indan-containing poly(diphenylacetylene) derivatives were synthesized. They had high molecular weights, good solubility in common organic solvents, and high thermal stability. These polymers exhibited very high gas permeability, although they have no bulky spherical substituents such as trimethylsilyl group. In particular, the oxygen permeability coefficients of fluorine-containing **2b** and **2e** reached 17 900 and 18 600 barrers, respectively, which are even larger than that of the most permeable PTMSP ever

Table 4. Gas Permeability Coefficient (*P*) of the Polymer Membranes[a]

	P (barrer) pure gas			*P* (barrer) mixed gas[b]		
membrane	CH_4	n-C_4H_{10}	Pn-C_4H_{10}/PCH_4	CH_4	n-C_4H_{10}	Pn-C_4H_{10}/PCH_4
2a	23 100	49 600	2.15	14 700	221 000	15.0
2b	33 000	50 000	1.52	24 400	245 000	10.0

[a] In the units of 1×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) (= 1 barrer), measured at 1.4 atm and 25 °C. [b] A 2 mol % n-C_4H_{10} mixture with CH_4.

Scheme 2. Synthesis of Indan-Containing Diphenylacetylene Monomers



reported. Furthermore, polymers **2a** and **2b** showed excellent performance for the removal of higher hydrocarbons from natural gas. The results in the present study provide valuable information on the future design of highly gas-permeable polymeric materials.

Experimental Section

General Data. Tantalum(V) chloride ($TaCl_5$, Aldrich) was used without further purification. Tetra-*n*-butyltin (*n*-Bu_4Sn, Wako) was used after distillation. Cyclohexane, benzene, and dichloromethane were distilled from calcium hydride under dry nitrogen prior to use. α-Methylstyrene (Aldrich), *tert*-butyl alcohol (Aldrich), 4-methylphenylacetylene (Wako), 4-fluoroiodobenzene (Aldrich), 3-fluoroiodobenzene (Aldrich), 2-fluoroiodobenzene (Aldrich), 3,4-difluoroiodobenzene (Aldrich), 3,5-difluoroiodobenzene (Aldrich), 4-chloroiodobenzene (Aldrich), and 4-bromoiodobenzene (Aldrich) were used as received without further purification. *p*-(Trimethylsilyl)phenylacetylene was donated by NOF Corp. 1,1,3,3-Tetramethylindan,[14] 1,1,2,2,3,3-hexamethylindan,[15] and 5-iodoindan[16] were prepared according to the literature methods. Monomers were synthesized referring to the literature concerning iodination[17] and ethynylation[18] (Scheme 2).

Molecular weights of polymers were estimated by gel permeation chromatography (GPC) on a Shimadzu PU/SPD-6A/UV-975 chromatograph equipped with polystyrene columns (Showa Denko Shodex K-805, K-806, and K-807) using $CHCl_3$ as an eluent at a flow rate of 1.0 mL/min, calibrated with polystyrene standard. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. NMR spectra were recorded on a JEOL EX-400 spectrometer. Melting points were measured with a Yanaco micro melting point apparatus. Elemental analysis of monomers was carried out at the Microanalytical Center of Kyoto University. Thermogravimetric analysis (TGA) was conducted in air with a Shimadzu TGA-50 thermal analyzer.

1-(1,1,3,3-Tetramethylindan-5-yl)-2-phenylacetylene (1a). A 300 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. After the flask was flushed with nitrogen, 1,1,3,3-tetramethylindan (16.4 g, 94 mmol), iodine (9.5 g, 37 mmol), and periodic acid (4.3 g, 19 mmol) was dissolved in aqueous acetic acid solution (100 mL, 80%) containing sulfuric acid (3.0 mL). The reaction mixture was stirred at 80 °C for 20 h. After H_2O (200 mL) was added, the solution was extracted with diethyl ether. The organic layer was washed first with 1 M aqueous $Na_2S_2O_3 \cdot 5H_2O$ (200 mL × 5) and then with H_2O (200 mL × 3).

The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give 5-iodo-1,1,3,3-tetramethylindan as a colorless liquid; yield 20%. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.50 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H, Ar), 7.42 (d, J = 1.6 Hz, 1H, Ar), 6.87 (d, J = 8.0 Hz, 1H, Ar), 1.81 (s, 2H, CH_2), 1.28 (s, 6H, CH_3), 1.28 (s, 6H, CH_3). ^{13}C NMR (CDCl$_3$) δ (ppm): 153.9, 151.0, 135.6, 131.9, 124.7, 91.8, 56.3, 42.6, 42.4, 31.4, 31.3.

A 300 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. After the flask was flushed with nitrogen, 5-iodo-1,1,3,3-tetramethylindan (5.6 g, 19 mmol), dichlorobis(triphenylphosphine)palladium (0.070 g, 0.10 mmol), cuprous iodide (0.11 g, 0.58 mmol) and triphenylphosphine (0.10 g, 0.38 mmol) were placed in the flask and dissolved in triethylamine (100 mL) at room temperature. Then, a solution of phenylacetylene (2.6 g, 25 mmol) in triethylamine (20 mL) was added dropwise, and stirring was continued at room temperature for 5 h. After that, triethylamine in the reaction mixture was evaporated off, and then ether (200 mL) was added to the residual mass. The solvent-insoluble solid was filtered off, and the filtrate was washed with 1 M aqueous HCl and then with water (3 × 200 mL).

The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give a colorless liquid; yield 80%. IR (KBr, cm^{-1}): 2958, 2360, 1597, 1493, 1315, 1065, 891, 829, 756, 690, 521. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.54−7.51 (m, 2H, Ar), 7.30−7.38 (m, 5H, Ar), 7.09 (d, J = 8.0 Hz, 1H, Ar), 1.92 (s, 2H, CH_2), 1.32 (s, 6H, CH_3), 1.31 (s, 6H, CH_3). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.9, 151.4, 131.5, 130.4, 128.3, 128.0, 125.9, 123.6, 122.6, 121.4, 90.1, 88.3, 56.5, 42.6, 42.5, 31.4, 31.3. Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.93; H, 8.26.

1-(1,1,3,3-Tetramethylindan-5-yl)-2-(4-fluorophenyl)acetylene (1b). A 500 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. After the flask was flushed with nitrogen, 5-iodo-1,1,3,3-tetramethylindan (7.8 g, 26 mmol), dichlorobis(triphenylphosphine)palladium (0.18 g, 0.26 mmol), cuprous iodide (0.29 g, 1.5 mmol) and triphenylphosphine (0.27 g, 1.0 mmol) were placed in the flask and dissolved in triethylamine (150 mL) at room temperature. Then, a solution of trimethylsilylacetylene (3.4 g, 35 mmol) in triethylamine (30 mL) was added dropwise, and stirring was continued at room temperature for 5 h. After that, triethylamine in the reaction mixture was evaporated off, and then ether (200 mL) was added to the residual mass. The solvent-insoluble solid was filtered off, and the filtrate was washed with water (3 × 200 mL). The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give 1-(1,1,3,3-tetramethylindan-5-yl)-2-(trimethylsilyl)acetylene as a white solid; yield 80%. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.30 (d, J = 8.0 Hz, 1H, Ar), 7.22 (s, 1H, Ar), 7.02 (d, J = 8.0 Hz, 1H, Ar), 1.89 (s, 2H, CH_2), 1.28 (s, 6H, CH_3), 1.27 (s, 6H, CH_3), 0.24 (s, 9H, SiCH_3).

Sodium hydroxide (1.0 g, 25 mmol) was added to a solution of 1-(1,1,3,3-tetramethylindan-5-yl)-2-(trimethylsilyl)acetylene (6.9 g, 26 mmol) in ethanol (200 mL) and water (20 mL), and the solution was stirred overnight at room temperature. After that, ether (200 mL) was added. The solvent-insoluble solid was filtered off, and the filtrate was washed with saturated aqueous NaCl (3 × 200 mL). The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give 1-(1,1,3,3-tetramethylindan-5-yl)acetylene as a colorless liquid; yield 80%. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.32 (d, J = 8.0 Hz, 1H, Ar), 7.25 (s, 1H, Ar), 7.06 (d, J = 8.0 Hz, 1H, Ar), 3.01 (s, 1H, ’CH), 1.91 (s, 2H, CH_2), 1.29 (s, 12H, CH_3). ^{13}C NMR (CDCl$_3$) δ (ppm): 152.4, 151.4, 130.9, 126.5, 122.5, 120.2, 84.4, 75.9, 56.4, 42.6, 42.5, 31.4, 31.3.

A 300 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. After the flask was flushed with nitrogen, 1-fluoro-4-iodobenzene (5.6 g, 25 mmol), dichlorobis(triphenylphosphine)palladium (0.14 g, 0.20 mmol), cuprous iodide (0.23 g, 1.2 mmol) and triphenylphosphine (0.21 g, 0.80 mmol) were placed in the flask and dissolved in triethylamine (150 mL) at room temperature. Then, a solution of 1-(1,1,3,3-tetramethylindan-5-yl)acetylene (3.9 g, 20 mmol) in triethylamine (20 mL) was added dropwise, and stirring was continued at room temperature for 5 h. After that, triethylamine in the reaction mixture was evaporated off, and then ether (200 mL) was added to the residual mass. The solvent-insoluble solid was filtered off, and the filtrate was washed with 1 M HCl aq. and then with water (3 × 200 mL). The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give a white solid; yield 79%, mp 112.0−113.0 °C. IR (KBr, cm^{-1}): 2958, 1598, 1508, 1453, 1363, 1228, 1156, 1092, 897, 834, 528. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.51−7.48 (m, 2H, Ar), 7.36 (d, J = 8.0 Hz, 1H, Ar), 7.28 (s, 1H, Ar), 7.10−7.00 (m, 3H, Ar), 1.92 (s, 2H, CH_2), 1.32 (s, 6H, CH_3), 1.30 (s, 6H, CH_3). ^{13}C NMR (CDCl$_3$) δ (ppm): 162.3 (d, J = 249 Hz), 152.0, 151.5, 133.4 (d, J = 8.2 Hz), 130.3, 125.8, 122.6, 121.2, 119.7, 115.6 (d, J = 21 Hz), 89.8, 87.2, 56.4, 42.7, 42.5, 31.4, 31.3. Anal. Calcd for $C_{21}H_{21}F$: C, 86.26; H, 7.24. Found: C, 86.52; H, 7.46.

1-(1,1,3,3-Tetramethylindan-5-yl)-2-(3-fluorophenyl)acetylene (1c). This monomer was prepared by the same method as for monomer **1b** using 3-fluoroiodobenzene instead of 4-fluoroiodobenzene to give a white solid; yield 90%, mp 32.5−33.5 °C. IR (KBr, cm^{-1}): 2954, 1576, 1491, 1264, 1204, 1123, 951, 870, 829, 791, 682, 519. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.37 (d, J = 8.0 Hz, 1H, Ar), 7.29 (s, 3H, Ar), 7.21 (d, J = 8.0 Hz, 1H, Ar), 7.09 (d, J = 8.0 Hz, 1H, Ar), 7.01 (s, 1H, Ar), 1.92 (s, 2H, CH_2), 1.32 (s, 6H, CH_3), 1.31 (s, 6H, CH_3). ^{13}C NMR (CDCl$_3$) δ (ppm): 162.4 (d, J = 246 Hz), 152.3, 151.5, 130.4, 129.8 (d, J = 9.1 Hz), 127.4 (d, J = 3.3 Hz), 126.0, 125.5 (d, J = 9.9 Hz), 122.6, 120.9, 118.3 (d, J = 22 Hz), 115.3 (d, J = 21 Hz), 91.1, 87.0, 56.4, 42.7, 42.5, 31.4, 31.3. Anal. Calcd for $C_{21}H_{21}F$: C, 86.26; H, 7.24. Found: C, 85.99; H, 7.31.

1-(1,1,3,3-Tetramethylindan-5-yl)-2-(2-fluorophenyl)acetylene (1d). This monomer was prepared by the same method as for monomer **1b** using 2-fluoroiodobenzene instead of 4-fluoroiodobenzene to give a colorless liquid; yield 81%. IR (KBr, cm^{-1}): 2956, 1497, 1450, 1364, 1266, 1222, 1098, 889, 828, 755, 518. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.50 (t, J = 8.0 Hz, 1H, Ar), 7.39 (d, J = 8.0 Hz, 1H, Ar), 7.31−7.27 (m, 2H, Ar), 7.12−7.06 (m, 3H, Ar), 1.92 (s, 2H, CH_2), 1.31 (s, 6H, CH_3), 1.30 (s, 6H, CH_3). ^{13}C NMR (CDCl$_3$) δ (ppm): 162.6 (d, J = 251 Hz), 152.3, 151.4, 133.4, 130.5, 129.6 (d, J = 8.2 Hz), 126.0, 123.9 (d, J = 4.1 Hz), 122.6, 121.0, 115.4 (d, J = 22 Hz), 112.2 (d, J = 16 Hz), 95.2 (d, J = 3.3 Hz), 81.5, 56.4, 42.7, 42.5, 31.4, 31.3. Anal. Calcd for $C_{21}H_{21}F$: C, 86.26; H, 7.24. Found: C, 86.41; H, 7.27.

1-(1,1,3,3-Tetramethylindan-5-yl)-2-(3,4-difluorophenyl)acetylene (1e). This monomer was prepared by the same method as for monomer **1b** using 3,4-difluoroiodobenzene instead of 4-fluoroiodobenzene to give a white solid; yield 91%. mp 70.5−71.5 °C. IR (KBr, cm^{-1}): 2956, 1600, 1514, 1276, 1200, 957, 875, 820, 772, 519. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.36−7.25 (m, 4H, Ar), 7.15−7.09 (m, 2H, Ar), 1.92 (s, 2H, CH_2), 1.32 (s, 6H, CH_3), 1.31 (s, 6H, CH_3). ^{13}C NMR (CDCl$_3$) δ (ppm): 152.4, 151.6, 150.4 (dd, ^{1}J = 249 Hz, ^2J = 12 Hz), 150.0 (dd, ^{1}J = 249 Hz, ^2J = 12 Hz), 130.4, 128.1 (dd, ^3J = 6.2 Hz, ^4J = 3.3 Hz), 126.0, 122.7, 120.7, 120.5 (dd, ^3J = 7.4 Hz, ^4J = 4.1 Hz), 120.4 (d, ^2J = 18 Hz), 117.4 (d, ^2J = 17 Hz), 90.6, 86.2, 56.4, 42.7, 42.5, 31.4, 31.3. Anal. Calcd for $C_{21}H_{21}F$: C, 81.26; H, 6.49. Found: C, 81.52; H, 6.60.

1-(1,1,3,3-Tetramethylindan-5-yl)-2-(3,5-difluorophenyl)acetylene (1f). This monomer was prepared by the same method as for monomer **1b** using 3,5-difluoroiodobenzene instead of 4-fluoroiodobenzene to give a white solid; yield 67%. mp 68.0−69.0 °C. IR (KBr, cm^{-1}): 2955, 2223, 1614, 1489, 1349, 1119, 987, 900, 857, 829, 520. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.36 (d, J = 8.0 Hz, 1H, Ar), 7.28 (s, 1H, Ar), 7.10 (d, d, J = 8.0 Hz, 1H, Ar), 7.03−7.03 (m, 2H, Ar), 6.80−6.75 (m, 1H, Ar), 1.93 (s, 2H, CH_2), 1.32 (s, 6H, CH_3), 1.31 (s, 6H, CH_3). ^{13}C NMR (CDCl$_3$) δ (ppm): 162.6

(dd, $^2J = 249$ Hz, $^3J = 13$ Hz), 152.7, 151.6, 130.5, 126.3 (t, $^3J = 12$ Hz), 126.1, 122.7, 120.4, 114.4 (dd, $^2J = 19$ Hz, $^4J = 7.4$ Hz), 104.1 (t, $^2J = 26$ Hz), 92.2, 86.1, 56.4, 42.7, 42.5, 31.4, 31.3. Anal. Calcd for $C_{21}H_{21}F$: C, 81.26; H, 6.49. Found: C, 81.04; H, 6.56.

1-(1,1,3,3-Tetramethylindan-5-yl)-2-(4-chlorophenyl)acetylene (1 g). This monomer was prepared by the same method as for monomer **1b** using 4-chlorophenylacetylene and 5-iodo-1,1,3,3-tetramethylindan instead of 1-(1,1,3,3-tetramethylindan-5-yl)acetylene and 1-fluoro-4-iodobenzene to give a white solid; yield 81%, mp 69.5−70.5 °C. IR (KBr, cm^{-1}): 2957, 2929, 2860, 1493, 1396, 1362, 1087, 1012, 889, 826, 523. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.44 (d, $J = 8.0$ Hz, 2H, Ar), 7.37−7.28 (m, 4H, Ar), 7.09 (d, $J = 8.0$ Hz, 1H, Ar), 1.92 (s, 2H, CH_2), 1.31 (s, 6H, CH_3), 1.30 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 152.2, 151.5, 133.9, 132.7, 130.3, 128.6, 125.9, 122.6, 122.1, 121.0, 91.1, 87.2, 56.4, 42.7, 42.5, 31.4, 31.3. Anal. Calcd for $C_{21}H_{21}Cl$: C, 81.67; H, 6.85. Found: C, 81.43; H, 6.82.

1-(1,1,3,3-Tetramethylindan-5-yl)-2-(4-bromophenyl)acetylene (1 h). This monomer was prepared by the same method as for monomer **1b** using 4-bromophenylacetylene and 5-iodo-1,1,3,3-tetramethylindan instead of 1-(1,1,3,3-tetramethylindan-5-yl)acetylene and 1-fluoro-4-iodobenzene to give a white solid; yield 71%, mp 86.0−87.0 °C. IR (KBr, cm^{-1}): 2594, 1490, 1463, 1390, 1363, 1296, 1138, 1069, 1009, 891, 830, 763, 524. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.48−7.45 (m, 2H, Ar), 7.39−7.35 (m, 3H, Ar), 7.28 (s, 1H, Ar), 7.09 (d, $J = 8.0$ Hz, 1H, Ar), 1.92 (s, 2H, CH_2), 1.31 (s, 6H, CH_3), 1.30 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 152.2, 151.5, 133.0, 131.5, 130.3, 125.9, 122.6, 122.5, 122.1, 121.0, 91.3, 87.2, 56.4, 42.7, 42.5, 31.4, 31.3. Anal. Calcd for $C_{21}H_{21}Br$: C, 71.39; H, 5.99. Found: C, 71.12; H, 5.93.

1-(1,1,3,3-Tetramethylindan-5-yl)-2-(4-methylphenyl)acetylene (1i). This monomer was prepared by the same method as for monomer **1b** using 4-methylphenylacetylene and 5-iodo-1,1,3,3-tetramethylindan instead of 1-(1,1,3,3-tetramethylindan-5-yl)acetylene and 1-fluoro-4-iodobenzene to give a white solid; yield 71%, mp 43.0−44.0. IR (KBr, cm^{-1}): 2957, 1512, 1484, 1455, 1362, 1294, 1181, 1116, 886, 832, 817, 529. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.43−7.35 (m, 3H, Ar), 7.28 (s, 1H, Ar), 7.14 (d, $J = 8.0$ Hz, 2H, Ar), 7.08 (d, $J = 8.0$ Hz, 1H, Ar), 2.36 (s, 3H, CH_3), 1.92 (s, 2H, CH_2), 1.31 (s, 6H, CH_3), 1.30 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 151.7, 151.4, 138.0, 131.4, 130.3, 129.1, 125.8, 122.5, 121.6, 120.5, 89.4, 88.4, 56.5, 42.6, 42.5, 31.4, 31.3, 21.5. Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.70; H, 8.63.

1-(1,1,3,3-Tetramethylindan-5-yl)-2-(4-trimethylsilylphenyl)acetylene (1j). This monomer was prepared by the same method as for monomer **1b** using *p*-(trimethylsilyl)phenylacetylene and 5-iodo-1,1,3,3-tetramethylindan instead of 1-(1,1,3,3-tetramethylindan-5-yl)acetylene and 1-fluoro-4-iodobenzene to give a white solid; yield 51%, mp 52.5−54.0. IR (KBr, cm^{-1}): 2955, 1594, 1485, 1363, 1249, 1103, 837, 756, 715, 670, 626, 534. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.49 (s, 4H, Ar), 7.38 (d, $J = 8.0$ Hz, 1H, Ar), 7.30 (s, 1H, Ar), 7.09 (d, $J = 8.0$ Hz, 1H, Ar), 1.92 (s, 2H, CH_2), 1.32 (s, 6H, CH_3), 1.31 (s, 6H, CH_3), 0.27 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$) δ (ppm): 151.9, 151.4, 140.6, 133.2, 130.6, 130.4, 125.9, 123.9, 122.6, 121.4, 90.5, 88.5, 56.5, 42.6, 42.5, 31.4, 31.3, −1.2. Anal. Calcd for $C_{22}H_{24}$: C, 83.17; H, 8.72. Found: C, 83.18; H, 8.89.

1-(1,1,2,2,3,3-Hexamethylindan-5-yl)-2-phenylacetylene (1k). 5-Iodo-1,1,2,2,3,3-hexamethylindan was prepared by the same method as for 5-iodo-1,1,3,3-tetramethylindan using 1,1,2,2,3,3-hexamethylindan instead of 1,1,3,3-tetramethylindan to give a white solid; yield 90%, mp 72.5−74.0 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.50 (dd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, 1H, Ar), 7.42 (d, $J = 1.6$ Hz, 1H, Ar), 6.88 (d, $J = 8.0$ Hz, 1H, Ar), 1.18 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 0.86 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 153.3, 150.3, 135.6, 131.9, 124.8, 91.6, 48.5, 47.8, 47.5, 27.3, 27.2, 21.4. Monomer **1k** was prepared by the same method as for monomer **1a** using 5-iodo-1,1,2,2,3,3-hexamethylindan instead of 5-iodo-1,1,3,3-tetramethylindan to give a white solid; yield 85%, mp 136−138 °C. IR (KBr, cm^{-1}): 2981, 2950, 1597, 1493, 1373, 1111, 887, 833, 756, 690, 532. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.54−7.51 (m, 2H, Ar), 7.39−7.30 (m, 5H, Ar), 7.10 (d, $J = 8.0$ Hz, 1H, Ar), 1.18 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 0.86 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 151.2, 150.7, 131.5, 130.3, 128.3, 127.9, 126.0, 123.6, 122.7, 121.2, 90.2, 88.2, 48.5, 47.8, 47.6, 27.3, 27.2, 21.4. Anal. Calcd for $C_{23}H_{26}$: C, 91.34; H, 8.66. Found: C, 91.57; H, 8.72.

1-(Indan-5-yl)-2-phenylacetylene (1 L). This monomer was prepared by the same method as for monomer **1a** using 5-iodoindan instead of 5-iodo-1,1,3,3-tetramethylindan to give a white solid; yield 77%, mp 56.0−57.0. IR (KBr, cm^{-1}): 2921, 1594, 1493, 1440, 1316, 913, 868, 822, 754, 689, 523. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.53−7.50 (m, 2H, Ar), 7.40−7.33 (m, 5H, Ar), 7.19 (d, $J = 8.0$ Hz, 1H, Ar), 2.92−2.89 (m, 4H, CH_2), 2.12−2.04 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ (ppm): 144.8, 144.4, 131.5, 129.6, 128.3, 128.0, 127.5, 124.3, 123.6, 120.7, 90.1, 88.2, 32.9, 32.6, 25.3. Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.72; H, 6.71.

1-(Indan-5-yl)-2-(4-trimethylsilylphenyl)acetylene (1m). This monomer was prepared by the same method as for monomer **1a** using 5-iodoindan and *p*-(trimethylsilyl)phenylacetylene instead of 5-iodo-1,1,3,3-tetramethylindan and phenylacetylene to give a white solid; yield 75%, mp 66.5−67.5. IR (KBr, cm^{-1}): 2954, 1589, 1485, 1389, 1246, 1099, 845, 752, 629, 532. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.48 (s, 4H, Ar), 7.40 (s, 1H, Ar), 7.31 (d, $J = 8.0$ Hz, 1H, Ar), 7.19 (d, $J = 8.0$ Hz, 1H, Ar), 2.92−2.89 (m, 4H, CH_2), 2.11−2.04 (m, 2H, CH_2), 0.27 [s, 9H, $Si(CH_3)_3$]. ^{13}C NMR ($CDCl_3$) δ (ppm): 144.8, 144.4, 140.6, 133.2, 130.6, 129.7, 127.5, 124.3, 123.9, 120.8, 90.5, 88.4, 32.9, 32.6, 25.3, −1.2. Anal. Calcd for $C_{20}H_{22}Si$: C, 82.70; H, 7.63. Found: C, 82.86; H, 7.74.

Polymerization. Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock at 80 °C for 24 h under dry nitrogen at the following reagent concentrations: $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM. The formed polymers were isolated by precipitation into a large amount of methanol, and dried to constant weight; the polymer yields were determined by gravimetry.

Membrane Fabrication and Desilylation. Membranes (thickness ca. 80−120 μm) were fabricated by casting toluene solution of polymers (concentration ca. 0.50−1.0 wt %) onto a flat-bottomed Petri dish. Then, the dish was covered with a glass vessel to slow solvent evaporation (ca. 3−5 days). After membranes were prepared, they were immersed in methanol for 24 h and dried to constant weight at room temperature for 24 h. With reference to the method described in the literature,[5c−e] the desilylation reaction of polymer membrane **2m** was carried out using trifluoroacetic acid. A procedure of the desilylation reaction is as follows: a polymer membrane was immersed in a mixture of trifluoroacetic acid and water (volume ratio 9:1) at room temperature for 24 h. The desilylated membrane was immersed in water for 24 h, then washed with water to remove residual impurities, and dried to constant weight at room temperature for 24 h.

Measurement of Gas Permeabilities. Gas permeability coefficients (P) (Table 3) of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus equipped with a MKS Baratron detector at 25 °C. The downstream side of the membrane was evacuated to 0.3 Pa, while the upstream side was filled with a gas at about 1 atm (10^5 Pa), and the increase of pressure in the downstream receiving vessel was measured. The P values were calculated from the slopes of time-pressure curves in the steady state where Fick's law held.

The CH_4 and $n\text{-}C_4H_{10}$ pure and mixed gases permeabilities (Table 4) were measured using a constant pressure/variable volume apparatus as described previously.[19] A mass flow controller (MKS Model# 1179A23CSIBV, Wilmington, MA) was installed on the upstream side to regulate the residue flow rate. Helium was used to sweep the downstream side of the membrane and carry the permeate (i.e., CH_4 and $n\text{-}C_4H_{10}$) to a gas chromatograph (GC). The total flow rate on the downstream side (i.e., helium + permeate) was measured with a soap film flow meter. The measurement temperatures were 25 ± 0.1 °C. The P values were calculated as described in the literature.[4a]

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Supporting Information Available: Table giving original values of gas permeability coefficient based on two different membranes. This material is available free of charge via the Internet at http://pubs.acs.org.

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