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Synthesis, characterization, and high gas permeability of poly(diarylacetylene)s having fluorenyl groups

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Diarylacetylenes having fluorenyl groups and other substituents (trimethylsilyl, *t*-butyl, bromine, fluorine) (**1a**–**1**) were polymerized with $TaCl_5$–*n*-Bu_4Sn. Monomers **1a**–**l** produced high molecular weight polymers **2a**–**l** (M_w 5.1×10^5–1.3×10^6) in 12–59% yields. All of the polymers were soluble in common organic solvents, and gave tough free-standing membranes by the solution casting method. The onset temperatures of weight loss of polymers **2a**–**l** in air were over 400 °C, indicating considerably high thermal stability. All the polymer membranes showed high gas permeability; e.g., the oxygen permeability coefficient (PO_2) of **2a** was as large as 4800 barrers. Membrane **2d** possessing two fluorine atoms at *meta* and *para* positions of the phenyl ring showed the highest oxygen permeability ($PO_2 = 6600$ barrers) among the present polymers.

1. Introduction

Disubstituted acetylenes can be polymerized with group 5 and 6 transition metal catalysts to provide substituted polyacetylenes, which have alternating carbon–carbon double bonds along the main chain [1]. It is known that some of these polymers, especially those having bulky substituents, exhibit extremely high gas permeability among all the existing polymers [2]. For example, poly(1-trimethylsilyl-1-propyne) [poly(TMSP)], which is obtained by the polymerization of the corresponding monomer with Ta- and Nb-based catalysts, is soluble in common organic solvents, provides a free-standing membrane by solution casting, and shows extremely high gas permeability [2f,3]; its oxygen permeability coefficient (PO_2) reaches about 10 000 barrers [1 barrer = 1×10^{-10} cm^3 (STP) cm/(cm^2 s cm Hg)]. The high gas permeability of poly(TMSP) is attributable to the presence of microvoids in the polymer matrix based on the stiff main chain composed of alternating double bonds and the bulky spherical trimethylsilyl groups.

Poly(diphenylacetylene) derivatives are another important type of highly gas-permeable polymers. For instance, poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] [poly(TMSDPA)] exhibits high gas permeability as well as thermal stability [4]. The PO_2 value of this polymer is as high as 1500 barrers, which is ca. twice larger than that of the most gas-permeable rubbery polymer, poly(dimethylsiloxane) [poly(DMS)] [5], and the onset temperature of weight loss in air (T_0) is 420 °C [4], which is clearly higher than that of poly(TMSP) (300 °C) [3b]. The superior combination of high gas permeability and high thermal stability makes poly(diphenylacetylene)s as promising candidates for gas separation membranes.

In previous studies, we have investigated the synthesis and gas permeation properties of several poly(diarylacetylene)s [6]. The polymerization of 1-(2-fluorenyl)-2-(*p*-trimethylsilyl)phenylacetylene with $TaCl_5$–*n*-Bu_4Sn afforded a high molecular weight polymer, whose PO_2 value was as high as 1700 barrers [6b]. Quite recently we have found that indane-containing poly(diarylacetylene)s exhibit gas permeability comparable to that of poly(TMSP) [7]. Polymers containing fluorene moieties in the main chain or side chain have attracted much attention as potential materials for light-emitting diodes [8], thin film transistors [9], solar cells [10], and gas separation membranes [11]. The 9-position of fluorene can be easily substituted by various groups. Thus, it is interesting to synthesize polyacetylenes having substituted fluorenyl groups in the side chain and to study their gas permeation properties.

Here we report the polymerization of diarylacetylenes containing substituted fluorenyl groups (Scheme 1, **1a**–**l**), and the fabrication of free-standing membranes from resultant polymers (**2a**–**l**). Furthermore, the gas permeability and general properties of polymers **2a**–**l** were investigated.

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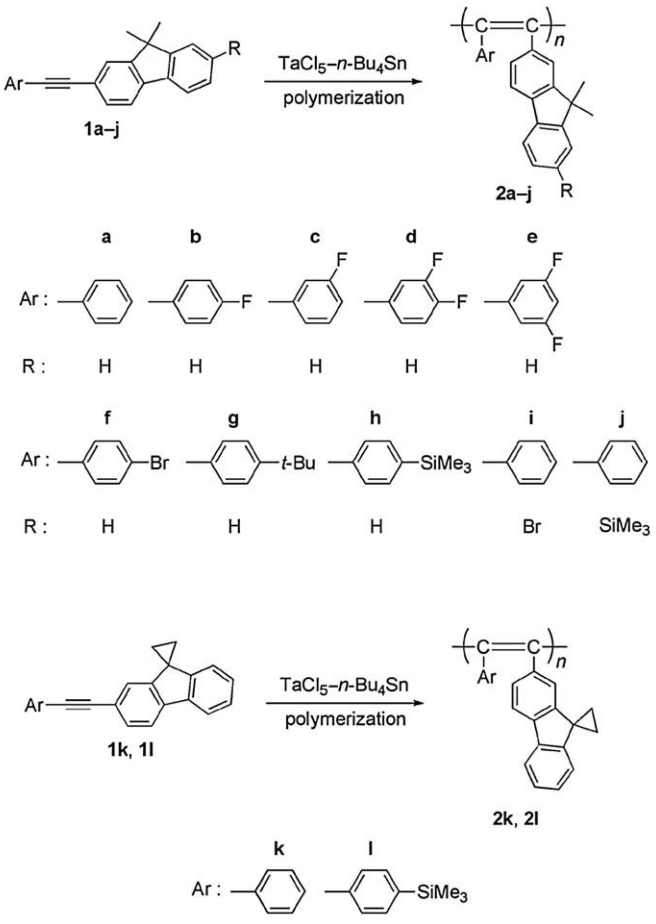


Scheme 1. Synthesis of poly(diarylacetylene)s having fluorenyl groups.

2. Experimental section

2.1. Measurements

Molecular weights of polymers were estimated by gel permeation chromatography ($CHCl_3$ as eluent, polystyrene calibration). IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were observed in $CDCl_3$ on a JEOL EX-400 spectrometer using tetramethylsilane as an internal standard. Elemental analysis of monomers was carried out at the Microanalytical Center of Kyoto University. Thermal gravimetric analysis (TGA) was conducted in air with a Shimadzu TGA-50 thermal analyzer. Melting points (mp) were determined on a Yanaco micro melting point apparatus.

2.2. Materials

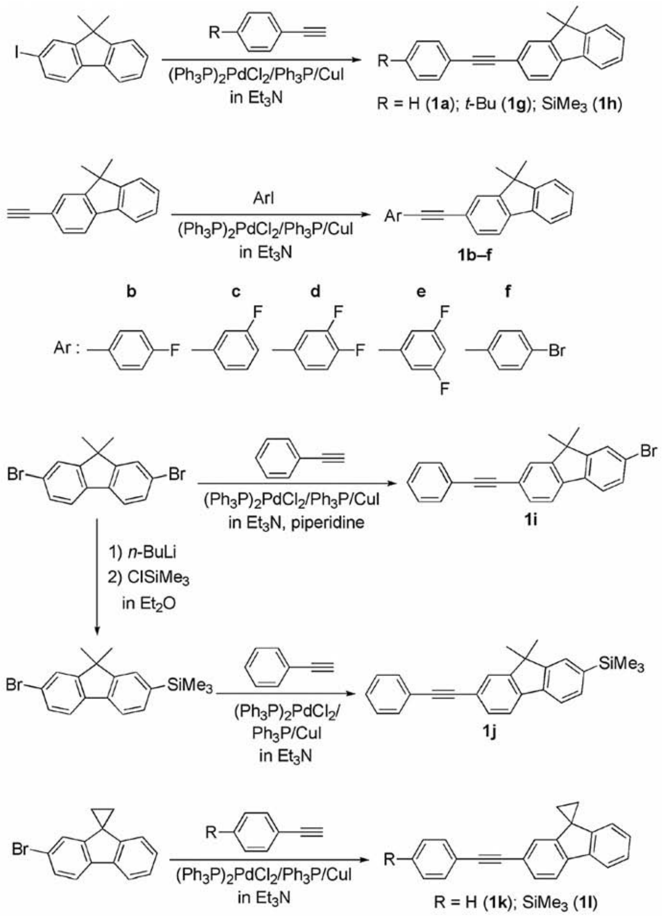
$TaCl_5$ (Aldrich) as main catalyst component was used without further purification. *n*-Bu_4Sn (Wako Pure Chemical) as cocatalyst was used after distillation. 4-(Trimethylsilyl)phenylacetylene was donated by NOF Co. Ltd. Fluorene, 2-bromofluorene, and 2,7-dibromofluorene were purchased from Aldrich. 4-*tert*-Butylphenylacetylene was commercially obtained from Wako Pure Chemical. Toluene as a polymerization solvent was purified by the standard method.

2.3. Monomer synthesis

9,9-Dimethyl-2-iodofluorene, 9,9-dimethyl-2,7-dibromofluorene, and 1-(9,9-dimethylfluoren-2-yl)acetylene were prepared according to the literature method [12]. 2′-Bromo-spiro(cyclopropane-1,9′-fluorene) was prepared according to the literature procedure [13]. Monomers **1a**–**l** were synthesized according to Scheme 2, referring to the literature with respect to the incorporation of the triple bond [14].

2.3.1. 1-Phenyl-2-(9,9-dimethylfluoren-2-yl)acetylene (*1a*)

A 500 mL three-necked flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar, and was flushed with dry nitrogen. 9,9-Dimethyl-2-iodofluorene (8.0 g, 25 mmol), bis(triphenylphosphine)palladium dichloride (0.18 g, 0.25 mmol), cuprous iodide (0.29 g, 1.5 mmol), triphenylphosphine (0.26 g, 1.0 mmol), and triethylamine (200 mL) were placed in the flask. Then, phenylacetylene (3.2 g, 31 mmol) in triethylamine (15 mL) solution was added dropwise, and the reaction mixture was stirred overnight at room temperature. After the triethylamine in the reaction mixture was evaporated, ether (ca. 300 mL) was added, and then the insoluble salt was filtered off. The filtrate was washed with 1 M hydrochloric acid and then with water. The ethereal solution was dried over anhydrous magnesium sulfate and then concentrated at reduced pressure. Purification of the crude product by silica gel column chromatography (eluent: hexane) provided the desired product. Yield 63%, white solid; mp 129.0–130.0 °C; IR (KBr, cm^{-1}): 2976, 2220, 1492, 1443, 1273, 1071, 882, 839, 756, 737, 692, 570. ^{1}H NMR ($CDCl_3$, ppm): 7.72–7.68 (m, 2H, Ar), 7.61 (s, 1H, Ar), 7.57–7.51 (m, 3H, Ar), 7.45–7.43 (m, 1H, Ar), 7.38–7.31 (m, 5H, Ar), 1.50 (s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 153.9, 153.6, 139.4, 138.5, 131.6, 130.7, 128.3, 128.1, 127.7, 127.1, 125.9,



Scheme 2. Synthesis of diarylacetylene monomers having fluorenyl groups.

123.4, 122.6, 121.7, 120.3, 119.9, 90.2, 89.4, 46.8, 27.0. Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.55; H, 6.33.

2.3.2. 1-(4-Fluorophenyl)-2-(9,9-dimethylfluoren-2-yl)-acetylene (1b)

This monomer was prepared by the same method as for **1a** by using *p*-fluoroiodobenzene and 1-(9,9-dimethylfluoren-2-yl)acetylene instead of 9,9-dimethyl-2-iodofluorene and phenylacetylene to give a white solid; yield 84%, mp 147.0–148.5 °C. IR (KBr, cm^{-1}): 2962, 2220, 1895, 1596, 1506, 1216, 1156, 1090, 835, 734. ^1H NMR ($CDCl_3$, ppm): 7.72–7.67 (m, 2H, Ar), 7.59–7.43 (m, 5H, Ar), 7.36–7.32 (m, 2H, Ar), 7.07–7.02 (m, 2H, Ar), 1.50 (s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 162.4 (d, $^1J = 249$ Hz), 153.9, 153.6, 139.5, 138.4, 133.4 (d, $^3J = 9.10$ Hz), 130.7, 127.7, 127.1, 125.8, 122.6, 121.5, 120.3, 120.0, 119.5 (d, $^4J = 3.30$ Hz), 115.6 (d, $^2J = 22.3$ Hz), 89.9, 88.3, 46.8, 27.0. Anal. Calcd for $C_{23}H_{17}F$: C, 88.43; H, 5.49. Found: C, 88.39; H, 5.60.

2.3.3. 1-(3-Fluorophenyl)-2-(9,9-dimethylfluoren-2-yl)acetylene (1c)

This monomer was prepared by the same method as for **1b** by using *m*-fluoroiodobenzene instead of *p*-fluoroiodobenzene to give a white solid; yield 88%, mp 87.0–88.0 °C. IR (KBr, cm^{-1}): 2979, 2206, 1912, 1577, 1449, 1192, 860, 781, 735, 678. ^1H NMR ($CDCl_3$, ppm): 7.73–7.69 (m, 2H, Ar), 7.60 (s, 1H, Ar), 7.52 (d, $J = 7.9$ Hz, 1H, Ar), 7.44 (m, 1H, Ar), 7.35–7.24 (m, 5H, Ar), 7.04 (m, 1H, Ar), 1.50 (s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 162.4 (d, $^1J = 246$ Hz), 153.9, 153.6, 139.8, 138.4, 130.8, 129.9 (d, $^3J = 9.10$ Hz), 127.8, 127.4 (d, $^4J = 3.30$ Hz), 127.1, 126.0, 125.3 (d, $^3J = 9.09$ Hz), 122.6, 121.1, 120.3, 120.0, 118.3 (d, $^2J = 23.1$ Hz), 115.4 (d, $^2J = 20.7$ Hz), 91.2, 88.2 (d, $^4J = 3.30$ Hz), 46.8, 27.0. Anal. Calcd for $C_{23}H_{17}F$: C, 88.43; H, 5.49. Found: C, 88.50; H, 5.75.

2.3.4. 1-(3,4-Difluorophenyl)-2-(9,9-dimethylfluoren-2-yl)-acetylene (1d)

This monomer was prepared by the same method as for **1b** by using 1-iodo-3,4-difluorobenzene instead of *p*-fluoroiodobenzene to give a white solid; yield 88%, mp 105.0–106.5 °C. IR (KBr, cm^{-1}): 2975, 2210, 1913, 1597, 1517, 1273, 1116, 860, 759, 735. ^1H NMR ($CDCl_3$, ppm): 7.73–7.69 (m, 2H, Ar), 7.59 (s, 1H, Ar), 7.50 (d, $J = 8.0$ Hz, 1H, Ar), 7.44 (m, 1H, Ar), 7.38–7.25 (m, 4H, Ar), 7.14 (m, 1H, Ar), 1.50 (s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 153.9, 153.6, 150.4 (dd, $^1J = 251$ Hz, $^2J = 12.4$ Hz), 150.0 (dd, $^1J = 248$ Hz, $^2J = 12.4$ Hz), 139.8, 138.3, 130.7, 128.1 (dd, $^3J = 6.20$ Hz, $^4J = 3.73$ Hz), 127.8, 127.1, 125.9, 122.6, 120.9, 120.4 (d, $^2J = 18.2$ Hz), 120.3 (d, $^3J = 8.26$ Hz), 120.3, 120.0, 117.4 (d, $^2J = 19.0$ Hz), 90.8 (d, $^5J = 2.48$ Hz), 87.2 (vt, $J = 2.07$ Hz), 46.8, 26.9. Anal. Calcd for $C_{23}H_{16}F_2$: C, 83.62; H, 4.88. Found: C, 83.73; H, 5.12.

2.3.5. 1-(3,5-Difluorophenyl)-2-(9,9-dimethylfluoren-2-yl)-acetylene (1e)

This monomer was prepared by the same method as for **1b** by using 1-iodo-3,5-difluorobenzene instead of *p*-fluoroiodobenzene to give a white solid; yield 79%, mp 95.0–96.0 °C. IR (KBr, cm^{-1}): 2979, 2208, 1912, 1617, 1424, 1122, 989, 838, 736, 509. ^1H NMR ($CDCl_3$, ppm): 7.71–7.66 (m, 2H, Ar), 7.59 (s, 1H, Ar), 7.49 (d, $J = 7.8$ Hz, 1H, Ar), 7.43–7.41 (m, 1H, Ar), 7.35–7.31 (m, 2H, Ar), 7.06–7.04 (m, 2H, Ar), 6.80–6.75 (m, 1H, Ar), 1.48 (s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 162.7 (dd, $^1J = 249$ Hz, $^3J = 13.2$ Hz), 153.9, 153.7, 140.1, 138.3, 130.9, 127.9, 127.2, 126.2 (t, $^3J = 12.4$ Hz), 126.0, 122.7, 120.6, 120.4, 120.0, 114.4 (dd, $^2J = 19.8$ Hz, $^4J = 7.44$ Hz), 104.2 (t, $^2J = 24.8$ Hz), 92.3, 87.2 (t, $^4J = 3.30$ Hz), 46.9, 27.0. Anal. Calcd for $C_{23}H_{16}F_2$: C, 83.62; H, 4.88. Found: C, 83.59; H, 5.02.

2.3.6. 1-(4-Bromophenyl)-2-(9,9-dimethylfluoren-2-yl)-acetylene (1f)

This monomer was prepared by the same method as for **1b** by using *p*-bromoiodobenzene instead of *p*-fluoroiodobenzene to give a white solid; yield 77%, mp 145.0–147.0 °C. IR (KBr, cm^{-1}): 2958, 2220, 1905, 1490, 1066, 1009, 887, 735, 523. ^1H NMR ($CDCl_3$, ppm): 7.73–7.68 (m, 2H, Ar), 7.59 (s, 1H, Ar), 7.51–7.47 (m, 3H, Ar), 7.45–7.39 (m, 3H, Ar), 7.37–7.31 (m, 2H, Ar), 1.49 (s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 153.9, 153.6, 139.7, 138.4, 133.0, 131.6, 130.7, 127.8, 127.1, 125.9, 122.7, 122.4, 122.3, 121.3, 120.3, 120.0, 91.4, 88.4, 46.9, 27.0. Anal. Calcd for $C_{23}H_{17}Br$: C, 74.00; H, 4.59. Found: C, 74.12; H, 4.89.

2.3.7. 1-(4-Tert-butylphenyl)-2-(9,9-dimethylfluoren-2-yl)-acetylene (1g)

This monomer was prepared by the same method as for **1a** by using 4-*tert*-butylphenylacetylene instead of phenylacetylene to give a white solid; yield 35%, mp 177.5–179.5 °C. IR (KBr, cm^{-1}): 2959, 1506, 1445, 1396, 834, 782, 757, 736, 567. ^1H NMR ($CDCl_3$, ppm): 7.72–7.67 (m, 2H, Ar), 7.60 (s, 1H, Ar), 7.52–7.48 (m, 3H, Ar), 7.44–7.42 (m, 1H, Ar), 7.39–7.31 (m, 4H, Ar), 1.50 (s, 6H, $C(CH_3)_2$), 1.33 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 153.9, 153.6, 151.4, 139.2, 138.6, 131.3, 130.7, 127.6, 127.1, 125.9, 125.4, 122.6, 121.9, 120.4, 120.2, 119.9, 89.6, 89.6, 46.8, 34.8, 31.2, 27.0. Anal. Calcd for $C_{27}H_{26}$: C, 92.52; H, 7.48. Found: C, 92.24; H, 7.54.

2.3.8. 1-(4-Trimethylsilylphenyl)-2-(9,9-dimethylfluoren-2-yl)-acetylene (1h)

This monomer was prepared by the same method as for **1a** by using 4-(trimethylsilyl)phenylacetylene instead of phenylacetylene to give a white solid; yield 63%, mp 139.0–142.0 °C. IR (KBr, cm^{-1}): 2959, 2219, 1591, 1445, 1252, 1099, 824, 757, 633, 454. ^1H NMR ($CDCl_3$, ppm): 7.73–7.68 (m, 2H, Ar), 7.61 (s, 1H, Ar), 7.54–7.49 (m, 5H, Ar), 7.45–7.43 (m, 1H, Ar), 7.36–7.31 (m, 2H, Ar), 1.50 (s, 6H, $C(CH_3)_2$), 0.28 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 153.9, 153.6, 140.9, 139.4, 138.5, 133.2, 130.8, 130.6, 127.7, 127.1, 125.9, 123.7, 122.7, 121.7, 120.3, 119.9, 90.6, 89.6, 46.9, 27.0, –1.2. Anal. Calcd for $C_{26}H_{26}Si$: C, 85.19; H, 7.15. Found: C, 85.05; H, 7.24.

2.3.9. 1-Phenyl-2-(9,9-dimethyl-7-bromofluoren-2-yl)-acetylene (1i)

This monomer was prepared similarly to **1a** from 9,9-dimethyl-2,7-dibromofluorene to give a white solid; yield 37%, mp 149.5–150.5 °C. IR (KBr, cm^{-1}): 2978, 1442, 1400, 1257, 1073, 820, 751, 686, 466. ^1H NMR ($CDCl_3$, ppm): 7.65 (d, $J = 7.8$ Hz, 1H, Ar), 7.59–7.51 (m, 6H, Ar), 7.46 (d, $J = 8.0$ Hz, 1H, Ar), 7.39–7.33 (m, 3H, Ar), 1.49 (s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 155.9, 153.2, 138.3, 137.5, 131.6, 130.9, 130.3, 128.4, 128.3, 126.2, 125.9, 123.3, 122.2, 121.6, 121.5, 120.0, 90.0, 89.8, 47.1, 26.9. Anal. Calcd for $C_{23}H_{17}Br$: C, 74.00; H, 4.59. Found: C, 74.00; H, 4.67.

2.3.10. 1-Phenyl-2-(9,9-dimethyl-7-trimethylsilylfluoren-2-yl)-acetylene (1j)

A 300 mL three-necked flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar. After the flask was flushed with nitrogen, 9,9-dimethyl-2,7-dibromofluorene (10 g, 28 mmol), ether (100 mL), and benzene (40 mL) were added and cooled at 0 °C. At the same temperature, a hexane solution of *n*-butyllithium (18 mL, 1.6 M, 28 mmol) was added dropwise, and then the mixture was stirred for 2 h at room temperature. Then, a solution of trimethylchlorosilane (3.0 g, 28 mmol) in ether (10 mL) was added dropwise at 0 °C, and stirring was continued further for 5 h at room temperature. A small amount of water was added at 0 °C, and the reaction mixture was extracted with ether. The organic phase was washed with water, and dried over anhydrous magnesium sulfate. After ether was evaporated, the crude product was purified by silica gel column chromatography (eluent: hexane) to give 9,9-dimethyl-2-bromo-7-(trimethylsilyl)fluorene as a white solid.

1j was prepared similarly to **1a** by using 9,9-dimethyl-2-bromo-7-(trimethylsilyl)fluorene instead of 9,9-dimethyl-2-iodofluorene to give a white solid; yield 43%, mp 124.0–125.0 °C. IR (KBr, cm^{-1}): 2958, 1458, 1396, 1246, 1107, 825, 756, 690, 629, 462. ^{1}H NMR ($CDCl_3$, ppm): 7.70 (d, $J = 7.3$ Hz, 2H, Ar), 7.60–7.50 (m, 6H, Ar), 7.37–7.34 (m, 3H, Ar), 1.51 (s, 6H, $C(CH_3)_2$), 0.32 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 153.8, 153.0, 140.1, 139.4, 139.2, 132.2, 131.6, 130.7, 128.4, 128.1, 127.2, 125.9, 123.4, 121.8, 120.1, 119.6, 90.3, 89.5, 46.9, 27.1, −0.9. Anal. Calcd for $C_{26}H_{26}Si$: C, 85.19; H, 7.15. Found: C, 85.41; H, 7.25.

2.3.11. 1-Phenyl-2-(spiro[cyclopropane-1,9′-fluoren]-2′-yl)-acetylene (*1k*)

This monomer was prepared similarly to **1a** from 2′-bromo-spiro(cyclopropane-1,9′-fluorene) to give a white solid; yield 72%, mp 103.5–105.0 °C. IR (KBr, cm^{-1}): 3053, 3004, 2207, 1490, 1439, 1426, 951, 835, 745, 691, 473. ^{1}H NMR ($CDCl_3$, ppm): 7.81–7.76 (m, 2H, Ar), 7.55–7.51 (m, 3H, Ar), 7.36–7.27 (m, 5H, Ar), 7.21 (s, 1H, Ar), 7.03 (d, $J = 7.5$ Hz, 1H, Ar), 1.76–1.69 (m, 4H, CCH_2CH_2). ^{13}C NMR ($CDCl_3$, ppm): 148.5, 148.2, 140.0, 139.2, 131.5, 129.7, 128.3, 128.1, 127.2, 126.1, 123.4, 121.8, 121.2, 120.3, 119.9, 118.6, 90.3, 89.4, 29.4, 18.4. Anal. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found: C, 94.52; H, 5.63.

2.3.12. 1-(4-Trimethylsilylphenyl)-2-(spiro[cyclopropane-1,9′-fluoren]-2′-yl)acetylene (*1l*)

This monomer was prepared by the same method as for **1k** by using 4-(trimethylsilyl)phenylacetylene instead of phenylacetylene to give a white solid; yield 61%, mp 142.5–144.0 °C. IR (KBr, cm^{-1}): 2954, 1592, 1426, 1250, 1098, 953, 841, 820, 752, 632. ^{1}H NMR ($CDCl_3$, ppm): 7.81–7.76 (m, 2H, Ar), 7.53–7.48 (m, 5H, Ar), 7.36–7.27 (m, 2H, Ar), 7.22 (s, 1H, Ar), 7.03 (d, $J = 7.3$ Hz, 1H, Ar), 1.77–1.69 (m, 4H, CCH_2CH_2), 0.27 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 148.5, 148.2, 140.9, 140.0, 139.2, 133.2, 130.6, 129.7, 127.2, 126.1, 123.7, 121.9, 121.3, 120.3, 119.9, 118.6, 90.7, 89.6, 29.4, 18.4, −1.2. Anal. Calcd for $C_{26}H_{24}Si$: C, 85.66; H, 6.64; Si, 7.70. Found: C, 85.70; H, 6.79.

2.4. Polymerization

Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. The polymerizations were carried out at 80 °C for 24 h under the following conditions: $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM. A detailed procedure of polymerization was as follows: a monomer solution was prepared in a Schlenk tube by mixing monomer **1a** (0.30 g) and toluene (3.0 mL). Another Schlenk tube was charged with $TaCl_5$ (36 mg), $n\text{-}Bu_4Sn$ (0.066 mL), and toluene (2.0 mL); this catalyst solution was aged at 80 °C for 10 min. Then the monomer solution was added to the catalyst solution. Polymerization was carried out at 80 °C for 24 h, which was quenched with a small amount of methanol. 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.

2.5. Membrane fabrication

Membranes (thickness ca. 50–80 μm) were fabricated by casting from toluene solution (**2a**–**e**, **2g**, **2h**, and **2j**–**l**) and chloroform solution (**2f** and **2i**) due to the difference in their solubility onto a flat-bottomed Petri dish (concentration ca. 0.80–1.5 wt%). Then, the dish was covered with a glass vessel to retard the rate of 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.

2.6. Measurement of gas permeabilities

Gas permeability coefficients of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus equipped with an MKS Baratron detector at 25 °C. The downstream side of the membrane was evacuated at 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 a downstream receiving vessel was measured. *P* values were calculated from the slopes of time-pressure curves in the steady state where Fick's law held.

3. Results and discussion

3.1. Polymerization

The polymerization of monomers **1a**–**l** having fluorenyl groups was carried out in toluene by using the $TaCl_5$–n-Bu_4Sn catalyst (Table 1). It is well known that the $TaCl_5$–n-Bu_4Sn catalyst is effective for the polymerization of diphenylacetylene derivatives, and provides polymers having high molecular weight [15], which is essential for the fabrication of free-standing membranes. Monomer **1a** afforded a polymer in a moderate yield (42%), whose M_w was as high as 5.9×10^5. Similarly, fluorine-containing monomers **1b**–**e** polymerized in ca. 40–60% yields into high molecular weight polymers ($M_w \geq 5.3 \times 10^5$). Monomers **1f**–**j** having bulky substituents also gave high molecular weight polymers. For instance, bromine-containing monomers **1f** and **1i** produced polymers with high M_w values (5.5×10^5 and 5.7×10^5, respectively) in 43% yield. Monomer **1g** having a *t*-butyl group produced a polymer with M_w (7.9×10^5) in a low yield (14%). Monomers **1h** and **1j** possessing a bulky trimethylsilyl group afforded polymers, whose M_w values reached 5.1×10^5 and 5.8×10^5, respectively, although the polymer yields were rather low (12 and 25%). Monomers **1k** and **1l** possessing a cyclopropane moiety at the C-9-position of fluorene polymerized practically in the same way as **1a**. Thus, all of polymers **2a**–**l** possessed enough high molecular weights for the fabrication of free-standing membranes. The appearance of these polymers was orange-colored and fibrous.

3.2. Solubility and thermal stability of the polymers

Solubility properties of polymers **2a**–**l** are summarized in Table 2. Polymers **2a**–**l** were all soluble in $CHCl_3$ and THF, and most of them were also soluble in toluene. The polymers having trimethylsilyl and *t*-butyl groups dissolved also in cyclohexane, while those with

Table 1
Polymerization of **1a**–**l** with $TaCl_5$–n-Bu_4Sn.[a]

Monomer	Polymer[b]		
	Yield (%)	$M_w \times 10^{-5}$ [c]	M_w/M_n[c]
1a	42	5.9	3.6
1b	49	13	3.9
1c	59	6.9	2.6
1d	40	6.7	2.2
1e	50	5.3	2.1
1f	43	5.5	2.3
1g	14	7.9	3.7
1h	12	5.1	4.5
1i	43	5.7	2.6
1j	25	5.8	2.2
1k	41	5.2	2.0
1l	47	9.0	2.8

[a] In toluene 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] Measured by GPC calibrated with polystyrenes as standards.

Table 2
Solubility of the polymers.[a]

Solvent	**2a**	**2b–d**	**2e**	**2f**	**2g,2h**	**2i**	**2j**	**2k**	**2l**
Hexane	−	−	−	−	−	−	+	−	−
Cyclohexane	±	−	−	−	+	−	+	−	−
Toluene	+	+	+	+	+	±	+	+	+
$CHCl_3$	+	+	+	+	+	+	+	+	+
THF	+	+	+	+	+	+	+	+	+
DMF	+	+	+	+	−	+	−	+	−
DMSO	−	−	+	−	−	−	−	−	−
Methanol	−	−	−	−	−	−	−	−	−

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

halogens tended to dissolve in *N*,*N*-dimethylformamide (DMF), a polar solvent. All the present polymers were insoluble in methanol. Due to the difference in their solubility, free-standing membranes were fabricated from either toluene (**2a**–**e**, **2g**, **2h**, and **2j**–**l**) or $CHCl_3$ (**2f** and **2i**) solution. The formed membranes were sufficiently tough, stiff, red, and transparent.

The thermal stability of polymers **2a**–**l** was examined by TGA in air (Fig. 1). The onset temperatures of weight loss (T_0) of **2a**–**l** were all above 400 °C, indicating considerably high thermal stability. When Si-containing polymers **2h**, **2j**, and **2l** were heated above 700 °C in air, the ash composed of SiO_2 remained, whose amounts agreed with the expected values.

3.3. *Gas permeability*

The gas permeability of membranes **2a**–**l** to various gases was examined at 25 °C (Table 3). The oxygen permeability coefficient (PO_2) of **2a** was as large as 4800 barrers. We previously synthesized poly[1-(2-fluorenyl)-2-(*p*-trimethylsilyl)phenylacetylene] (**2m**) without two methyl groups at 9-position of the fluorenyl group and its desilylated polymer **3m** (Chart 1) [6b]. Their PO_2 values were 1700 and 2200 barrers, respectively. These results indicate that the oxygen permeability is remarkably enhanced by introducing two methyl groups into polymer **2m**. The reason for the high gas permeability of **2a** is probably that the two methyl groups, sticking out vertically from the rigid fluorene plane, inhibit the effective π-stacking between aromatic rings, generating a large amount of molecular-scale void in the membrane. Similar and even more obvious effects of plural numbers of methyl groups have been observed in our recent studies of poly(diarylacetylene)s having polymethylated indanyl groups [7], although a polymer having the 9,9,10,10-tetramethyl-9,10-dihydroanthracene moiety did not show so high gas permeability [16].

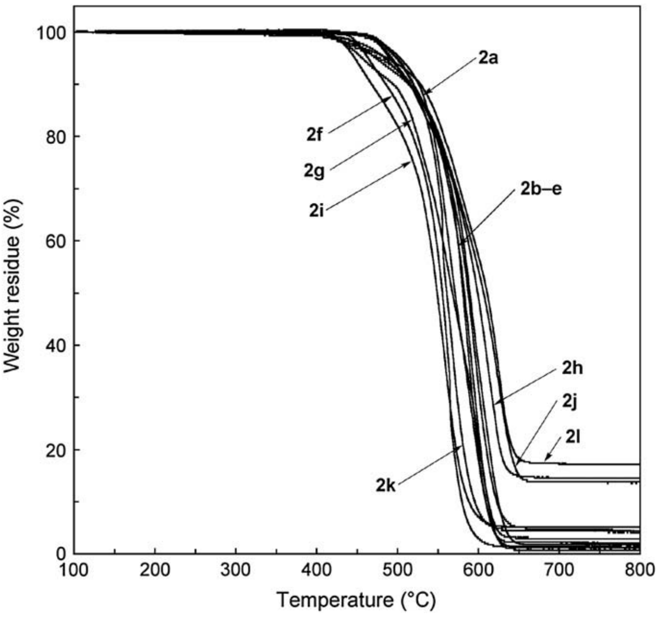


Fig. 1. TGA curves of the polymers (in air, heating rate 10 °C/min).

Table 3
Gas permeability coefficients (*P*) of the polymer membranes.

Polymer	*P* (barrer[a])						PO_2/PN_2
	He	H_2	O_2	N_2	CO_2	CH_4	
2a	3200	8100	4800	3300	17000	9100	1.5
2b	4600	11000	6200	4700	21000	11000	1.3
2c	4100	9900	5900	4200	18000	11000	1.4
2d	5000	11000	6600	5100	26000	12000	1.3
2e	2100	5000	2700	1700	9200	4200	1.6
2f	3400	8700	5000	3500	17000	9300	1.4
2g	2700	6200	3500	2500	11000	6600	1.4
2h	520	1100	470	210	1900	550	2.2
2i	1500	3700	2000	1100	8000	3000	1.8
2j	3400	8500	5400	3400	18000	10000	1.6
2k	600	1400	660	300	3200	810	2.2
2l	840	1900	1000	540	4100	1500	1.9
2m[b]	1300	3100	1700	950	6500	2000	1.7
3m[b]	1600	3700	2200	1300	8500	2400	1.7

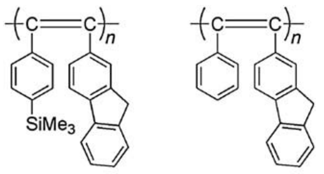
[a] At 25 °C in the units of 1×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) (=1 barrer) (the values are average values of the two independent observed values using two different membranes).

[b] Data from Ref. [6b].

Fluorine-containing polymers tended to display even higher oxygen permeability; namely, the PO_2 values of **2b**–**d** were clearly larger than that of **2a**, and **2d** possessing two fluorine atoms at *meta* and *para* positions exhibited the highest permeability among the present polymers ($PO_2 = 6600$ barrers). Thus, it can be said that incorporation of F atoms into poly(diarylacetylene)s is effective to enhance the gas permeability of the membranes [19]. The reason why polymer **2e** showed lower permeability might be that the *m*,*m*-difluorophenyl group is more planar and tends to stack with one another.

Polymer **2f** having bromine atoms also displayed high gas permeability ($PO_2 = 5000$ barrers), while **2g** having *t*-butyl groups showed somewhat lower gas permeability ($PO_2 = 3500$ barrers). Furthermore, **2h** having trimethylsilyl groups exhibited the lowest gas permeability within this series ($PO_2 = 470$ barrers), which was only one tenth of that of **2a**. This implies that a bulkier spherical substituent rather lowers the gas permeability in this type of polymers.

Polymers having the same substituents at different positions showed different PO_2 values. For example, the PO_2 value of bromine-containing polymer **2i** was 2000 barrers, which was much lower than that of **2f** ($PO_2 = 5000$ barrers), while polymer **2j** possessing trimethylsilyl groups exhibited much higher gas permeability ($PO_2 = 5400$ barrers) than that of **2h** ($PO_2 = 470$ barrers). Polymers **2k** and **2l** containing cyclopropane moiety showed rather



2m **3m**

Chart 1. Structures of **2m** and **3m**.

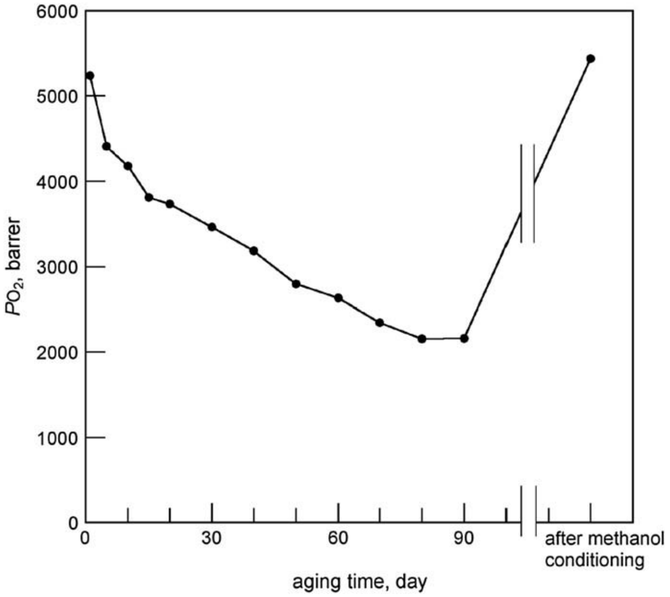


Fig. 2. Effect of aging time on the oxygen permeability of **2a** (stored at 25 °C in air).

low gas permeability; the PO_2 values of **2k** and **2l** remained 660 and 1000 barrers, respectively. The gas permeability difference between **2a** and **2k** suggests that the rotational motion of methyl groups plays an important role to enhance gas permeability, which agrees with the results of dynamic neutron scattering [20]. The permeability of **2a**–**l** to other gases such as He, H_2, N_2, CO_2, and CH_4 showed similar tendencies. The separation factors of oxygen against nitrogen (PO_2/PN_2) of polymers **2a**–**l** were in a range of 1.3–2.2, where a tradeoff is observed between permeability and permselectivity, namely, more permeable polymers are generally less selective and vice versa [21].

The time dependence of oxygen permeability of **2a** (thickness: ca. 80 μm) was examined by storing the membrane at 25 °C in air. As seen in Fig. 2, the PO_2 value of **2a** gradually decreased with time to become a half of the initial value after 60 days, and it decreased further to 2000 barrers after 90 days and almost leveled off. On the other hand, the PO_2/PN_2 value of **2a** gradually increased from 1.43 to 1.84 after 90 days. Similar tendencies have been observed with other disubstituted acetylene polymers. For instance, the PO_2 value of poly(TMSP) decreases from ca. 5000 to ca. 100 barrers after about 100 days [22], and that of poly[1-β-naphthyl-2-(*p*-trimethylsilyl)-phenylacetylene] decreases from 3500 to 1000 barrers after 90 days [6c]. The decreased PO_2 value of **2a** was completely restored to the initial value when the membrane was immersed in methanol for 24 h.

4. Conclusions

A series of poly(diarylacetylene)s having fluorenyl groups (**2a**–**l**) were synthesized by the polymerization of the corresponding monomers. These polymers possessed high molecular weight, good solubility in organic solvents, and high thermal stability. All of the polymers gave free-standing membranes by solution casting, and exhibited high gas permeability. The PO_2 value of polymer **2a** was 4800 barrers, which is three times as large as that of poly(TMSDPA). Further, polymers containing both fluorenyl groups and fluorine atoms showed even larger oxygen permeability, and the value of **2d** reached 6600 barrers. The results in the present study indicate that the incorporation of both 9,9-dimethylfluorenyl groups and fluorine atoms achieves high gas permeability. These polymer membranes are thought to be promising candidates for gas separation membranes from the viewpoint of high gas permeability and high thermal stability.

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[16] We also synthesized 1-phenyl-2-(9,9,10,10-tetramethyl-9,10-dihydroanthracen-2-yl)acetylene (**1n**) according to the literature [14,17,18], and monomer **1n** produced a polymer (**2n**) with M_w (4.9 × 105) in 36% yield (Conditions; at 80 °C for 48 h, $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM). The PO_2 value of polymer **2n** was 1600 barrers. **1n**; white solid, mp 216.5–218.0 °C. IR (KBr, cm^{-1}): 3060, 3030, 2963, 2925, 2212, 1596, 1492, 1438, 1270, 1042, 896, 831, 755, 689, 568. ^1H NMR ($CDCl_3$, ppm): 7.71 (d, $^4J = 1.5$ Hz, 1H, Ar), 7.57–7.48 (m, 5H, Ar), 7.41 (dd, $^3J = 8.3$ Hz, $^4J = 1.7$ Hz, 1H, Ar), 7.37–7.24 (m, 5H, Ar), 1.69 (s, 6H, $C(CH_3)_2$), 1.67 (s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): 142.4, 142.1, 141.4, 141.3, 131.6, 130.2, 129.2, 128.3, 128.1, 126.9, 126.7, 126.7, 126.2, 126.1, 123.4, 120.9, 89.7, 88.6, 37.3, 37.2, 35.0, 34.8. Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.56; H, 7.36.

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