Synthesis and properties of various poly(diphenylacetylenes) containing *tert*-amine moieties

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ABSTRACT

The polymerization of diphenylacetylene derivatives possessing *tert*-amine moieties, such as triphenylamine, *N*-substituted carbazole and indole, was examined in the presence of TaCl$_5$–*n*-Bu$_4$Sn (1:2) catalyst. A polymer with high molecular weight ($M_w = 570 \times 10^3$) was obtained in good yield by the polymerization of diphenylamine-containing monomer **1b**, whereas the isopropylphenylamine derivative (**1c**) gave a polymer with relatively low molecular weight ($M_w = 2.4 \times 10^3$). The polymerization of monomer **1d** containing cyclohexylphenylamine group did not proceed; however, carbazolyl- and indolyl-containing monomers also produced polymers. Poly(**1b**), poly(**2f**) and poly(**4b**) could be fabricated into free-standing membranes by casting toluene solutions of these polymers. The gas permeability of poly(**1b**) was too low to be evaluated accurately whereas poly(**4b**) possessing two chlorine atoms in the repeating unit showed higher gas permeability than that of poly(**1b**); furthermore, poly(**2f**) having trimethylsilyl and 3-methylindolyl groups exhibited relatively high gas permeability ($P_{O_2} = 49$ barrers). In the cyclic voltammograms of diphenylamino group-containing polymers, poly(**1b**) and poly(**2b**), the intensities of oxidation and reduction peaks decreased more than those of carbazolyl-containing poly(**2a**). The molar absorptivity (ε) of poly(**1b**) at ~700 nm increased with increasing applied voltage in the UV–vis spectrum.

1. Introduction

Substituted polyacetylenes having a variety of pendants and stiff main chain composed of alternating double bonds are one of the most attractive classes of functionalized polymers, which exhibit interesting properties such as energy transfer, energy migration, gas permeability, and formation of helical conformation [1–6]. Unsubstituted polyacetylene is insoluble in common organic solvents and easily decomposes in air. On the other hand, substituted polyacetylenes feature excellent solubility, high thermal stability, facile fabrication of membranes, and high gas permeability [7–11].

The past few decades have witnessed extensive research activity for the synthesis and exploration of various properties of poly(diphenylacetylenes) [12–22]. For example, the free-standing membrane of poly(diphenylacetylene) bearing *p*-trimethylsilyl group shows remarkably high gas permeability ($P_{O_2} = 1500$ barrers) and high thermal stability [9,11]. Although tantalum catalysts are commonly used for the polymerization of diphenylacetylene derivatives, hydroxy-containing diphenylacetylenes do not polymerize with any of early transition metal catalysts

including tantalum, molybdenum, and tungsten due to their low tolerance against polar functional groups. However, the protection of hydroxy groups by sterically bulky silyl moieties such as *tert*-BuMe$_2$Si enables polymerization of oxygen-containing monomers, and deprotection of silyl groups after polymerization provides hydroxy-containing poly(diphenylacetylene)s [23–29]. The resultant polymers possessing hydroxy groups exhibit excellent CO$_2$ permselectivity due to high affinity of the hydroxy group for CO$_2$ molecules ($P_{CO_2} = 100$–300, $P_{CO_2}/P_{N_2} = 35$–45), thus are expected to serve as interesting candidates for CO$_2$ separation membranes.

Although the gas permeation properties of polyimides, a well-known class of polymers possessing nitrogen in the form of imide, have been extensively investigated, their gas permeability is relatively low [30–34]. On the other hand, there have been few reports regarding the gas permeability of substituted polyacetylenes bearing amino groups till today. Amino group-containing polymers are expected to show high CO$_2$ permselectivity as amino groups, due to their polar nature, have been reported to interact with the carbon dioxide molecules. Although introduction of nitrogen functionalities to poly(diphenylacetylene) may lead to novel membrane materials featuring both high gas permeability and remarkable permselectivity, proper selection of amino groups is a prerequisite to avoid the possible deactivation of TaCl$_5$ which otherwise shows high activity in the polymerization of

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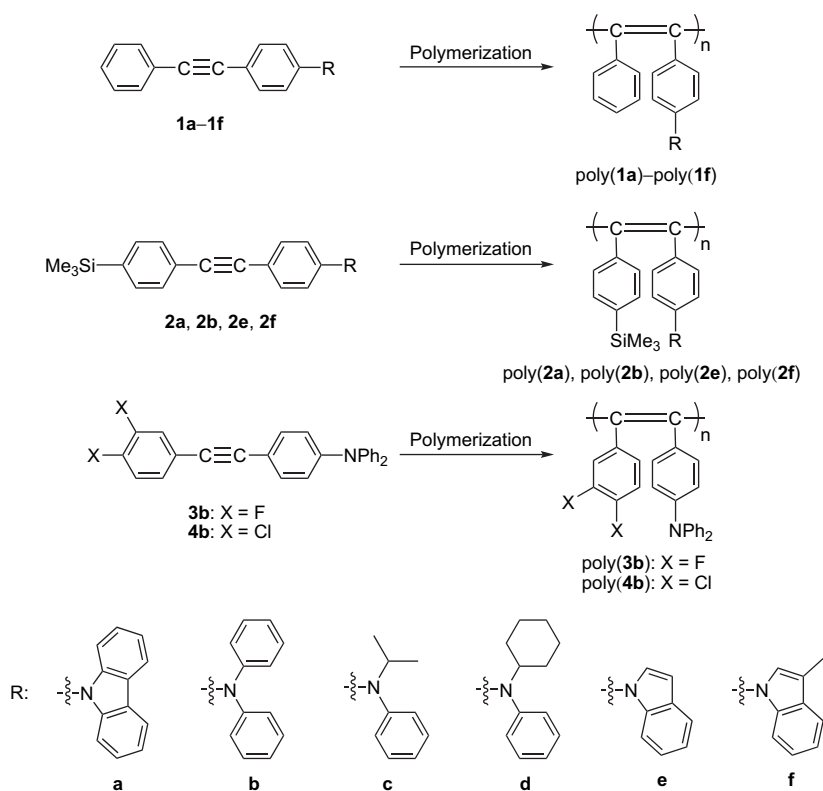
Scheme 1. Polymerization of monomers **1–4**.

diphenylacetylene derivatives. The only one example of poly-(diphenylacetylenes) bearing nitrogen-containing pendants/substituents is poly[1-(*p*-*N*-carbazolylphenyl)-2-phenylacetylene], whose oxygen permeability is too low to measure accurately [35].

Furthermore, conjugated aromatic amines such as carbazole and triphenylamine carry a lone-pair of electrons on nitrogen atom which undergoes a redox reaction to generate cation radical, hence they have been widely studied in the domains of electrochemistry, magnetism, etc. [36–41]. Polymers with these moieties are also well known to show interesting properties including hole transfer [42–45], electroluminescence [46,47], photoluminescence [48–51], and electrochromism [52,53].

This paper deals with the polymerization of several diphenylacetylenes carrying tertiary amine moieties as shown in Scheme 1. We prepared free-standing membranes of the resulting polymers and elucidated their general properties, gas permeability, and electrochromism. In general, tantalum-based metathesis catalysts are more or less sensitive to nitrogen-containing monomers, hence bulky substituent- and/or conjugated amine-bearing monomers were chosen to avoid the coordination of nitrogen atom with the metal center of catalyst.

2. Experimental

2.1. Measurements

The molecular weights of polymers were estimated by gel permeation chromatography (CHCl₃ as eluent, Showa Denko Shodex K-805, K-806, and K-807, polystyrene calibration). IR spectra were recorded on a Shimadzu FT/IR-4100 spectrophotometer. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in CDCl₃ on a JEOL EX-400 spectrometer. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to the resonances of the internal solvent and shown relative to tetramethylsilane (TMS). Thermogravimetric

analyses (TGA) were conducted in air with a Perkin–Elmer TGA7 thermal analyzer. Ultraviolet–visible (UV–vis) and emission spectra were measured on Jasco V-550 and FP-750 spectrophotometers, respectively. Melting points (mp) were determined on a Yanaco micro melting point apparatus. Elemental analysis was carried out at the Kyoto University Elemental Analysis Center. Cyclic voltammograms were measured on an HCH Instruments electrochemical analyzer ALS600A-n. The measurements were carried out with a modified ITO substrate as the working electrode coupled with a Pt plate counter and Ag/AgCl reference electrode, with a solution of a polymer (1 mM) and tetrabutylammonium perchlorate (TBAP, 0.1 M) in CH₂Cl₂. UV–vis spectra of polymer films under application of voltage were measured as follows. A polymer solution (0.2 M in CHCl₃) was spin coated on an ITO electrode at a spin rate of 1000 rpm, and the electrode was dried under vacuum at 50 °C for 16 h. It was immersed in a solution of TBAP (0.2 M) in acetonitrile in a quartz cell. UV–vis absorption spectra of the cell were recorded under application of voltage from 0 to 2500 mV with respect to an Ag/AgCl (saturated) reference electrode. The voltage was scanned anodically, and 5-min equilibration time was taken before each spectral scan to minimize the transient effect. The applied voltages reported herein were calibrated using ferrocene as a standard.

2.2. Materials and methods

TaCl₅ (Strem) as catalyst was used as received, while *n*-Bu₄Sn (Wako) as cocatalyst was purified by distillation before using. Phenylacetylene (Aldrich), triphenylamine (Aldrich), triethylamine (Wako), triphenylphosphine (Wako), copper iodide (Wako), Pd₂(dibenzylideneacetone)₃ (Pd₂(dba)₃, Aldrich), 1,4-bis(diphenylphosphino)ferrocene (dppf, Aldrich), carbazole (Aldrich), indole (Wako), 3-methylindole (Wako), sodium *tert*-butoxide (Wako), *N*-cyclohexyaniline (Wako), *N*-isopropylaniline (Wako), 1 M tetrabutylammonium fluoride (TBAF) solution in THF (Wako),

3,4-difluoroiodobenzene (Wako), 3,3-dichloroiodobenzene (Wako) and 4-bromoiodobenzene (Wako) were used without further purification. Toluene and cyclohexane as polymerization solvents were purified by distillation. 4-(Trimethylsilyl)phenylacetylene [54] and 4-bromophenyldiphenylamine [55] were prepared according to the literature procedures.

2.3. Synthesis of monomers

Monomers were synthesized according to Scheme 2 referring to the literature [56,57]. The details of the synthetic procedure and analytical data are as follows.

2.3.1. 1-(4-Bromophenyl)-2-phenylacetylene (5)

A 1 L three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar and flushed with nitrogen. 4-Bromoiodobenzene (25.0 g, 88.4 mmol), bis(triphenylphosphine)palladium dichloride (620 mg, 0.884 mmol), copper iodide (1.01 g, 5.30 mmol), triphenylphosphine (925 mg, 3.54 mmol), and triethylamine (500 mL) were placed in the flask. Then, phenylacetylene (9.03 g, 88.4 mmol) in triethylamine (20.0 mL) was added and the reaction mixture was stirred overnight at room temperature. After the triethylamine in the reaction mixture was evaporated, diethyl ether (500 mL) was added, and then the insoluble salt was filtered off. The solution was washed with 1 M hydrochloric acid (500 mL) and then with water (500 mL).
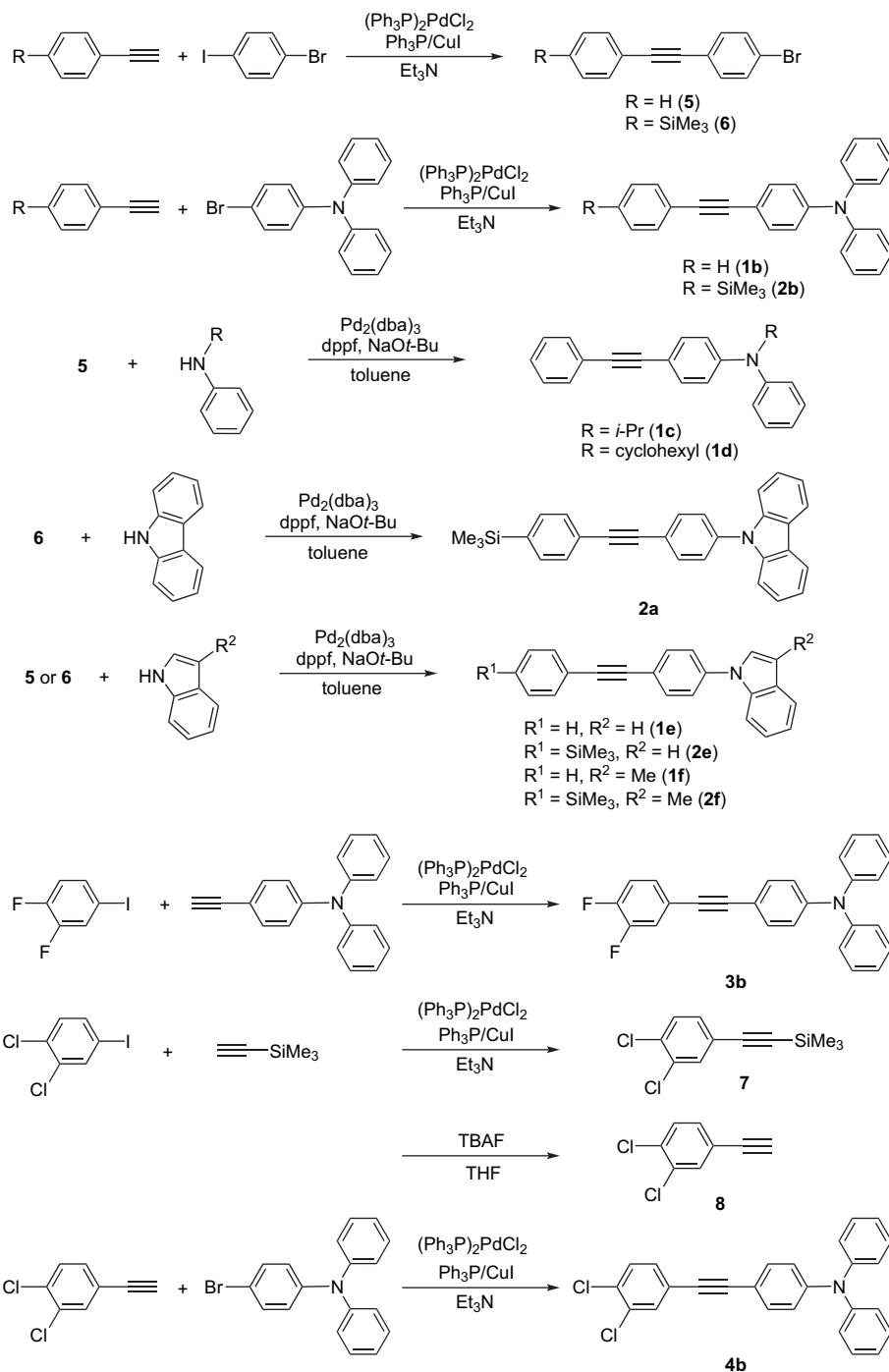
Scheme 2. Synthesis of monomers **1**–**4**.

The ethereal solution was dried over anhydrous sodium sulfate followed by the rotary evaporation of ether. The purification of the crude product by flash column chromatography (eluent: hexane) provided the desired product. Yield 96%, white solid. ^{1}H NMR (CDCl$_3$, ppm): 7.58–7.42 (m, 5H, Ar), 7.42–7.28 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$, ppm): 133.0, 131.6, 131.5, 128.5, 128.3, 122.9, 122.4, 122.2, 90.5, 88.3.

2.3.2. 1-(4-Bromophenyl)-2-(4-trimethylsilyl)phenylacetylene (**6**)

The compound was synthesized from 4-(trimethylsilyl)phenylacetylene in a manner similar to **5**. Yield 95%, white solid. ^{1}H NMR (CDCl$_3$, ppm): 7.55–7.42 (m, 6H, Ar), 7.37 (d, 2H, Ar), 0.27 (s, 9H, SiCH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 141.4, 133.2, 133.0, 131.6, 130.6, 123.1, 122.4, 122.3, 90.7, 88.7, −1.3.

2.3.3. 1-(4-N,N-Diphenylamino)phenyl-2-phenylacetylene (**1b**)

A 500 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar and was flushed with hydrogen. 4-Bromophenyldiphenylamine (13.0 g, 40.0 mmol), bis-(triphenylphosphine)palladium dichloride (140 mg, 0.200 mmol), copper iodide (229 mg, 1.20 mmol), triphenylphosphine (210 mg, 0.800 mmol), and triethylamine (300 mL) were placed in the flask. Then, phenylacetylene (4.09 g, 40.0 mmol) in triethylamine (20.0 mL) was added and the reaction mixture was stirred overnight. After the triethylamine in the reaction mixture was evaporated, ether (300 mL) was added, and then the insoluble salt was filtered off. The solution was washed with 1 N hydrochloric acid and then with water. The ethereal solution was dried over anhydrous sodium sulfate followed by the rotary evaporation of ether. The purification of the crude product by flash column chromatography (eluent: hexane) provided the desired product. Yield 46%, white solid; mp 103.5–104.5 °C; IR (KBr): 3052, 3036, 2202, 1586, 1488, 1321, 1279, 1176, 1071, 833, 755, 689 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.47 (d, 2H, Ar), 7.34 (d, 2H, Ar), 7.28–7.16 (m, 7H, Ar), 7.10–7.04 (m, 4H, Ar), 7.04–6.93 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$, ppm): 147.7, 147.0, 132.4, 131.9, 129.3, 128.2, 127.8, 124.8, 123.5, 122.3, 122.1, 116.0, 89.7, 88.6. Anal. Calcd for C$_{26}$H$_{19}$N: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.39; H, 5.64; N, 4.02.

2.3.4. 1-(4-N,N-Diphenylamino)phenyl-2-(4-trimethylsilyl)-phenylacetylene (**2b**)

The compound was synthesized from 4-(trimethylsilyl)phenyl-acetylene in a manner similar to **1a**. Yield 40%, pale yellow solid; mp 46.1–47.1 °C; IR (KBr): 3061, 3034, 2952, 2893, 2211, 1588, 1509, 1494, 1279, 1248, 1100, 838, 753, 695 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.26–7.18 (m, 4H, Ar), 7.15 (d, 2H, Ar), 7.05–6.91 (m, 4H, Ar), 6.90–6.80 (m, 4H, Ar), 6.80–6.68 (m, 4H, Ar), 0.28 (s, 9H, SiCH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 147.7, 147.1, 140.3, 133.1, 132.5, 130.5, 129.3, 124.8, 123.9, 123.4, 122.2, 116.1, 90.1, 88.9, −1.2. Anal. Calcd for C$_{29}$H$_{27}$NSi: C, 83.40; H, 6.52; N, 3.35. Found: C, 83.15; H, 6.78; N, 3.20.

2.3.5. 1-(4-N-Isopropyl-N-phenylamino)phenyl-2-phenyla-cetylene (**1c**)

A 300 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar and was flushed with nitrogen. 1-(4-Bromophenyl)-2-phenylacetylene (2.57 g, 10.0 mmol), Pd$_2$(dba)$_3$ (183 mg, 0.200 mmol), potassium *tert*-butoxide (1.92 g, 20.0 mmol), dppf (166 mg, 0.300 mmol) and toluene (100 mL) were placed in the flask. Then, *N*-isopropylaniline (1.35 g, 10.0 mmol) was added with a syringe and the reaction mixture was heated to reflux for 24 h. After cooling, the reaction solution was filtered off and the solid was washed with ether (50 mL). The solution was washed with water (200 mL) and the organic layer was dried over anhydrous sodium sulfate followed by the rotary evaporation of ether. Purification of the crude product by flash column chroma-tography (eluent: hexane) provided the desired product. Yield 41%,

white solid; mp 152.9–153.4 °C; IR (KBr): 2988, 2973, 2207, 1587, 1513, 1493, 1320, 1228, 1198, 1106, 821, 754, 707, 689 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.57–7.19 (m, 10H, Ar), 7.05 (d, 2H, Ar), 6.59 (d, 2H, Ar), 4.33 (sep, 1H, NCHMe$_2$), 1.16 (d, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 148.2, 143.0, 132.4, 131.2, 129.4, 128.9, 128.2, 127.4, 125.4, 120.5, 116.1, 111.9, 90.2, 87.6, 50.0, 20.9. Anal. Calcd for C$_{23}$H$_{21}$N: C, 88.71; H, 6.80; N, 4.50. Found: C, 88.52; H, 7.01; N, 4.51.

2.3.6. 1-(4-N-Cyclohexyl-N-phenylamino)phenyl-2-phenylacetylene (**1d**)

The compound was synthesized from *N*-isopropylaniline in a manner similar to **1c**. Yield 28%, white solid; mp 107.8–108.6 °C; IR (KBr): 3056, 3034, 2930, 2853, 2206, 1882, 1586, 1512, 1491, 1383, 1338, 1299, 1136, 1075, 818, 753, 706 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.47 (m, 2H, Ar), 7.42–7.17 (m, 8H, Ar), 7.02 (m, 2H, Ar), 6.54 (m, 2H, Ar), 3.85–3.78 (m, 1H, NCH◁), 2.05–0.85 (m, 10H, CH$_2$). ^{13}C NMR (CDCl$_3$, ppm): 148.3, 143.4, 132.4, 131.2, 129.4, 129.0, 128.1, 127.4, 125.5, 123.9, 115.8, 111.8, 90.4, 87.6, 56.8, 31.7, 26.1, 25.7. Anal. Calcd for C$_{26}$H$_{25}$N: C, 88.85; H, 7.17; N, 3.99. Found: C, 88.61; H, 7.25; N, 3.96.

2.3.7. 1-{4-(9-Carbazolyl)}phenyl-2-(4-trimethylsilyl)-phenylacetylene (**2a**)

The compound was synthesized from carbazole and **6** in a manner similar to **1c**. Yield 37%, pale brown solid; mp 169.0–170.0 °C; IR (KBr): 3419, 3049, 2952, 2893, 2216, 1924, 1592, 1515, 1452, 1314, 1232, 1099, 854, 838, 823, 750, 724 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 8.13 (d, 2H, Ar), 7.74 (d, 2H, Ar), 7.67–7.17 (m, 14H, Ar), 0.29 (s, 9H, SiCH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 142.3, 141.4, 134.2, 134.0, 131.6, 127.7, 126.9, 126.7, 124.4, 121.2, 121.1, 120.3, 111.4, 110.6, 91.4, 89.9, −0.3. Anal. Calcd for C$_{29}$H$_{25}$NSi: C, 83.81; H, 6.06; N, 3.37. Found: C, 83.43; H, 6.09; N, 3.65.

2.3.8. 1-{4-(1-Indolyl)}phenyl-2-phenylacetylene (**1e**)

The compound was synthesized from indole in a manner similar to **1c**. Yield 68%, white solid; mp 95.5–96.2 °C; IR (KBr): 3131, 3044, 2335, 1717, 1593, 1521, 1455, 1335, 1213, 1137, 840, 760, 744, 725, 688 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.75–7.00 (m, 14H, Ar), 6.57 (d, 1H, Ar). ^{13}C NMR (CDCl$_3$, ppm): 139.4, 135.5, 132.8, 131.6, 129.5, 128.4, 127.5, 123.8, 123.0, 122.6, 121.2, 121.1, 120.6, 110.5, 104.2, 90.1, 88.7. Anal. Calcd for C$_{22}$H$_{15}$N: C, 90.07; H, 5.15; N, 4.77. Found: C, 90.33; H, 5.26; N, 4.84.

2.3.9. 1-{4-(1-Indolyl)}phenyl-2-(4-trimethylsilyl)phenyl-acetylene (**2e**)

The compound was synthesized from indole and **6** in a manner similar to **1c**. Yield 93%, pale yellow solid; mp 125.0–126.0 °C; IR (KBr): 3062, 3025, 2950, 2893, 2216, 1922, 1592, 1518, 1454, 1335, 1248, 1210, 1132, 1102, 839, 741 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.70–7.38 (m, 10H, Ar), 7.35–7.10 (m, 3H, Ar), 6.68 (d, 1H, Ar), 0.31 (s, 9H, SiCH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 141.3, 139.5, 135.6, 133.3, 132.9, 130.7, 129.5, 127.6, 123.8, 123.3, 122.6, 121.2, 121.2, 120.6, 110.5, 104.2, 90.3, 89.0, −1.2. Anal. Calcd for C$_{25}$H$_{23}$NSi: C, 82.14; H, 6.34; N, 3.83. Found: C, 82.38; H, 6.49; N, 3.86.

2.3.10. 1-{4-(3-Methyl-1-indolyl)}phenyl-2-phenylacetylene (**1f**)

The compound was synthesized from 3-methylindole in a manner similar to **1c**. Yield 83%, white solid; mp 94.8–95.6 °C; IR (KBr): 3057, 3029, 2914, 2857, 2216, 1918, 1594, 1518, 1455, 1356, 1217, 1104, 840, 754, 736, 690 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.72–7.60 (m, 3H, Ar), 7.60–7.52 (m, 3H, Ar), 7.52–7.44 (m, 2H, Ar), 7.44–7.30 (m, 3H, Ar), 7.30–7.15 (m, 3H, Ar), 2.38 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 139.7, 135.7, 132.8, 131.6, 130.0, 128.4, 128.3, 125.0, 123.4, 123.1, 122.6, 120.5, 120.1, 119.3, 113.5, 110.4, 89.9, 88.8, 9.6. Anal. Calcd for C$_{23}$H$_{17}$N: C, 89.87; H, 5.57; N, 4.56. Found: C, 90.03; H, 5.69; N, 4.63.

2.3.11. 1-{4-(3-Methyl-1-indolyl)}phenyl-2-(4-trimethyl-silyl)phenylacetylene (2f)

The compound was synthesized from 3-methylindole and **6** in a manner similar to **1c**. Yield 52%, pale yellow solid; mp 134.2–135.2 °C; IR (KBr): 3062, 3012, 2958, 2913, 2856, 2212, 1912, 1592, 1515, 1456, 1388, 1241, 1101, 839, 739 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.70–7.41 (m, 10H, Ar), 7.27–7.10 (m, 3H, Ar), 2.38 (s, 3H, CH$_3$), 0.28 (s, 9H, SiCH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 141.2, 139.7, 135.7, 133.2, 132.9, 130.6, 130.0, 125.1, 123.4, 122.6, 120.6, 120.1, 119.3, 113.5, 110.4, 90.1, 89.2, 9.6. Anal. Calcd for C$_{26}$H$_{25}$NSi: C, 82.27; H, 6.64; N, 3.69. Found: C, 82.12; H, 6.92; N, 3.60.

2.3.12. 1-(4-N,N-Diphenylamino)phenyl-2-(3,4-difluorophenyl)acetylene (3b)

The compound was synthesized from 3,4-difluoroiodobenzene and 4-(N,N-diphenylamino)phenylacetylene in a manner similar to **1b**. Yield 50%, pale yellow solid; mp 106.2–107.2 °C; IR (KBr): 3064, 3037, 1893, 1592, 1516, 1489, 1416, 1265, 1102, 948, 872, 749, 698 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.36–7.15 (m, 8H, Ar), 7.15–7.01 (m, 7H, Ar), 7.01–6.94 (m, 2H, Ar). ^{13}C NMR (CDCl$_3$, ppm): 151.3 (dd), 148.6 (dd), 148.2, 147.0, 132.5, 129.4, 127.9 (dd), 125.1, 123.7, 122.0, 120.5 (dd), 120.2 (d), 117.4 (d), 115.1, 90.2, 86.4. Anal. Calcd for C$_{26}$H$_{17}$F$_2$N: C, 81.87; H, 4.49; N, 3.67. Found: C, 81.62; H, 4.77; N, 3.64.

2.3.13. 1-(3,4-Dichlorophenyl)-2-trimethylsilylacetylene (7)

The compound was synthesized from 3,4-dichloroiodobenzene and trimethylsilylacetylene in a manner similar to **1b**. Yield 96%, pale yellow solid. ^{1}H NMR (CDCl$_3$, ppm): 7.54 (s, 1H, Ar), 7.35 (d, 1H, Ar), 7.26 (d, 1H, Ar), 0.25 (s, 9H, SiCH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 133.5, 132.8, 132.4, 131.0, 130.2, 123.1, 102.4, 96.7, −0.2.

2.3.14. 3,4-Dichlorophenylacetylene (8)

Compound **7** (16 g, 66 mmol) was dissolved in THF (400 mL), and aq. 1 M TBAF in THF (66 mL) was added to the solution. The resulting mixture was stirred overnight. THF was removed by evaporation, and the residue was dissolved in ether (250 mL) and washed with water (250 mL × 3). The organic layer was dried over anhydrous MgSO$_4$, and concentrated by rotary evaporation to give pale yellow liquid. It was purified by silica gel column chromatography eluting with hexane. Yield 42%, colorless liquid. ^{1}H NMR (CDCl$_3$, ppm): 7.57 (s, 1H, Ar), 7.39 (d, 1H, Ar), 7.27 (d, 1H, Ar), 3.14 (s, 1H, ≡CH). ^{13}C NMR (CDCl$_3$, ppm): 133.8, 133.4, 132.6, 131.2, 130.4, 122.0, 81.3, 79.2.

2.3.15. 1-(4-N,N-Diphenylamino)phenyl-2-(3,4-dichlorophenyl)acetylene (4b)

The compound was synthesized from **8** and 4-bromo-N,N-diphenylaniline in a manner similar to **1b**. Yield 26%, pale yellow solid; mp 152.8–153.8 °C; IR (KBr): 3035, 2222, 2193, 1584, 1508, 1486, 1281, 1179, 1121, 1028, 877, 841, 819, 755, 695 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.63–7.50 (d, 1H, Ar), 7.44–7.15 (m, 9H, Ar), 7.15–7.12 (m, 5H, Ar), 7.12–6.88 (m, 2H, Ar). ^{13}C NMR (CDCl$_3$, ppm): 148.3, 147.0, 132.9, 132.5, 132.4, 130.5, 130.3, 129.4, 125.1, 124.1, 123.7, 123.6, 121.9, 114.9, 91.8, 86.3. Anal. Calcd for C$_{26}$H$_{17}$Cl$_2$N: C, 75.37; H, 4.14; N, 3.38. Found: C, 75.17; H, 4.27; N, 3.20.

2.4. Polymerization

Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen at 80 °C for 24 h under the following conditions: $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, $[n\text{-Bu}_4\text{Sn}] = 40$ mM. The detailed procedure of polymerization is as follows: A monomer solution was prepared in a Schlenk tube by mixing monomer **1b** (138 mg) and toluene (1.0 mL). Another Schlenk tube was charged with TaCl$_5$ (14 mg), n-Bu$_4$Sn (26 μL), and toluene (1.0 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 resulting polymer was isolated by precipitation into a large excess of methanol and its yield was determined by gravimetry.

2.5. Membrane fabrication

Membranes (thickness ca. 100 μm) of poly(**1b**), poly(**2a**), poly(**2b**), poly(**2f**), poly(**3b**), and poly(**4b**) were fabricated by casting toluene solution of the polymers (concentration ca. 1.0 wt%) onto a flat-bottomed Petri dish. The dish was covered with a glass vessel to retard the rate of solvent evaporation (ca. 3–5 days).

3. Results and discussion

3.1. Polymerization

The polymerization of diphenylacetylenes **1** and **2** having amine moiety was carried out in toluene with TaCl$_5$–n-Bu$_4$Sn (Table 1). Monomer **1b** bearing diphenylamino group polymerized in 73% yield with a weight-average molecular weight of 570×10^3 (run 1). The polymerization of monomer **1c**, substituted with isopropylphenylamino group, also proceeded successfully and a polymer with $M_w = 2.4 \times 10^3$ was obtained (run 2). In contrast, cyclohexylphenylamine-substituted monomer **1d** did not polymerize (run 3). Monomer **1b** provided the corresponding polymer with a very high molecular weight probably because the three conjugated phenyl groups decrease the electron density on the nitrogen atom to avoid the complexation and deactivation of the active species. On the other hand, monomer **1c** has two conjugated phenyl groups and moreover an electron-donating isopropyl group, which caused increase of the electron density on the nitrogen atom. This seems to have led to the lower yield and molecular weight of poly(**1c**) than those of poly(**1b**). Furthermore, cyclohexyl group of monomer **1d**, which is a stronger electron-donating group than isopropyl group, completely suppressed the polymerizability. Diphenylacetylenes carrying conjugated indole and 3-methylindole moieties (**1e** and **1f**) did polymerize but the obtained polymers were insoluble in common organic solvents (runs 4 and 5). Monomers **2a**, **2b**, **2e**, and **2f**, which have a trimethylsilyl group on one phenyl ring and an aromatic amino group on the other, were also examined. Monomer **2b** polymerized in a slightly lower yield than that of **1b**, and poly(**2b**) possessed a somewhat lower molecular weight, which are probably due to the steric bulk of trimethylsilyl substituent (run 7). Poly(**2e**) and poly(**2f**) were obtained in high yield, and poly(**2f**) was soluble in toluene and CHCl$_3$, whereas poly(**2e**) was insoluble in these solvents due to the absence of methyl group in the indolyl

Table 1
Polymerization of monomers **1–4**[a]

| Run | Monomer | Polymer[c] | | |
		Yield, %	$M_w \times 10^{-3}$[d]	M_w/M_n[d]
1	**1b**	73	570	3.6
2	**1c**	59	2.4	2.5
3	**1d**	0	–	–
4	**1e**	94	Insoluble	
5	**1f**	93	Insoluble	
6	**2a**	55	1500	4.2
7	**2b**	61	520	4.1
8	**2e**	73	Insoluble	
9	**2f**	65	>6000	–
10[b]	**3b**	50	1100	1.5
11	**4b**	67	570	1.3

[a] In toluene, 80 °C, 48 h; $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, $[n\text{-Bu}_4\text{Sn}] = 40$ mM.
[b] For 120 h.
[c] Methanol-insoluble part.
[d] Estimated by GPC (THF, PSt).

substituent (runs 8 and 9). Monomer **3b** bearing two fluorine atoms gave a polymer in 19% yield after 48 h, and the polymer yield was improved (50%) by extending the polymerization time to 120 h (run 10). Monomer **4b** having two chlorine atoms polymerized in 67% yield after 48 h (run 11).

To examine the relationship of the monomer structure and polymerizability, the electron densities on nitrogen atoms of monomers **1a**–**1f** were calculated by the semiempirical molecular orbital method, MOPAC, AM1 Hamiltonian, running on Spartan'06, Windows. The order of the electron density on nitrogen atoms of monomers is: **1e** (0.29 e) < **1f** (0.30 e) < **1a** (0.47 e) < **1b** (0.52 e) < **1c** (0.78 e) < **1d** (0.83 e). It terms out that the electron density has a direct bearing on the polymer yield of poly(**1b**)–poly(**1f**); namely, the lower the electron density on the nitrogen atom, the higher the polymer yield. For instance, monomers **1c** and **1d** differ only slightly in terms of the steric bulk but their polymerizability is quite different from each other (Table 1), most probably being strongly affected by the electron density on the nitrogen atom.

3.2. Gas permeation properties of polymers

The fabrication of free-standing membranes of high molecular weight polymers, poly(**1b**), poly(**2a**), poly(**2b**), poly(**2f**), poly(**3b**), and poly(**4b**), was attempted by casting their toluene solution, and gas permeation properties of the membranes were elucidated (Table 2). The free-standing membranes fabricated from poly(**1b**), poly(**2f**), and poly(**4b**) had adequate strength to render gas permeability measurements possible but unfortunately those from poly(**2a**), poly(**2b**), and poly(**3a**) were too brittle. Poly(**1b**) showed low gas permeability (e.g., $P_{O_2} = 3.6$ barrers) and permeability coefficients for nitrogen, carbon dioxide, and methane could not be determined. Poly(**1a**) also exhibited small gas permeability coefficients, which is probably due to the favored packing of polymer chains ensuing from the high planarity of the carbazolyl group. Poly(**4b**) possessing two chlorine atoms on the phenyl ring without the amine moiety in poly(**1b**), exhibited improved gas permeability which can be attributed to the increase of the number/size of molecular voids caused by electron repulsion between halogen atoms, as reported for poly[*p*-(trimethylsilyl)diphenylacetylene] derivatives [15]. Poly(**2f**) bearing 3-methylindolyl and trimethylsilyl groups exhibited higher gas permeability than poly(**1b**) and poly(**4b**), presumably originating from the high local mobility of trimethylsilyl group. The P_{N_2} and P_{CO_2} values of poly(*p*-adamantyldiphenylacetylene) are 16 and 29 barrers ($P_{CO_2}/P_{N_2} = 1.8$), respectively [58], and those of poly[1-(*n*-hexylthio)-1-propyne] are 14 and 150 barrers ($P_{CO_2}/P_{N_2} = 11$), respectively [59]. Meanwhile, those of nitrogen-containing poly(**4b**) synthesized in this paper were 14 and 255 barrers ($P_{CO_2}/P_{N_2} = 18$), respectively, where high CO_2 separation performance should have emanated from high affinity of CO_2 for polar amine moiety.

3.3. Thermal properties of polymers

TGA curves of the polymers measured in air are shown in Fig. 1. All the polymers exhibited excellent thermal stability and the onset
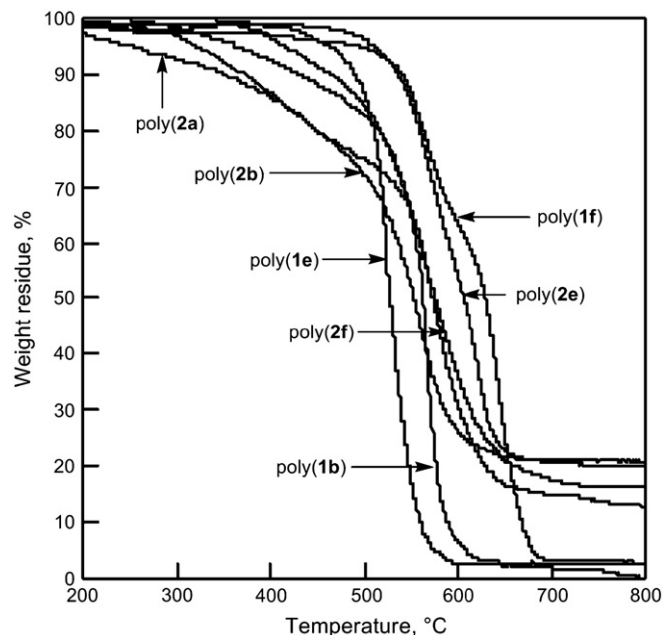
Table 2
Gas permeability coefficients (P) of polymer membranes[a]

Membrane	P (barrer)						P_{O_2}/P_{N_2}	P_{CO_2}/P_{N_2}
	He	H_2	O_2	N_2	CO_2	CH_4		
Poly(**1b**)	23	37	3.6	_[b]	_[b]	_[b]	_[b]	_[b]
Poly(**2f**)	108	185	49	14	255	32	3.5	18
Poly(**4b**)	29	45	8.6	1.9	55	3.4	4.5	29

[a] At room temperature in the units of 1×10^{-10} cm^3 (STP) cm/(cm^2) (s) (cmHg) (=1 barrer).
[b] Could not be determined due to low gas permeability.

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

temperatures of weight loss (T_0) were in the range of 200–500 °C. Upon heating the polymers, substituted with trimethylsilyl group, above 600 °C about 15% of residue remained, which is attributable to SiO_2 resulting from the oxidation of the silyl group.

3.4. UV–vis and fluorescence spectra of polymers

The UV–vis spectra of triphenylamine- or carbazole-containing polymers were measured in chloroform (Fig. 2). All the polymers exhibited absorption maxima around 300 nm due to the nitrogen-containing aromatic groups and weaker absorptions or shoulders in the range of 350–500 nm assignable to the main chain conjugation.
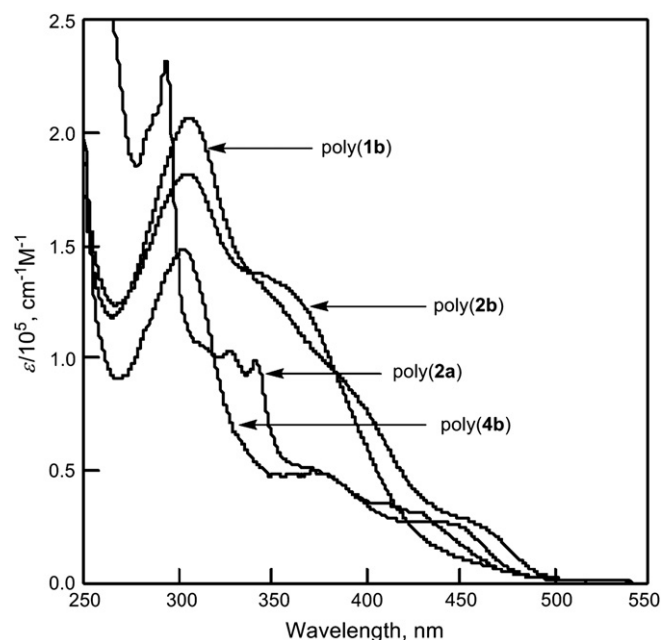

Fig. 2. UV–vis spectra of poly(**1b**), poly(**2a**), poly(**2b**), and poly(**4b**) (measured in CHCl$_3$, concentrations: poly(**1b**): 5.8×10^{-5} M, poly(**2a**): 4.8×10^{-5} M, poly(**2b**): 2.4×10^{-5} M, poly(**4b**): 2.4×10^{-5} M).
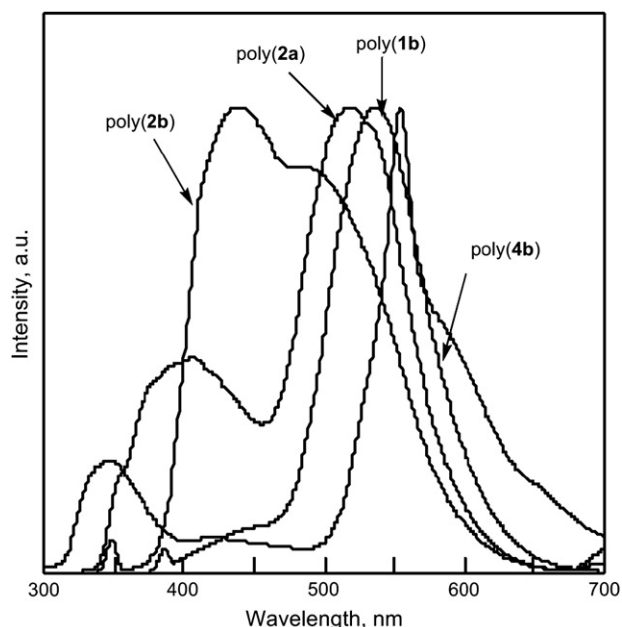
Fig. 3. Fluorescence spectra of polymers (measured in CHCl₃, excited at 389 nm for poly(**1b**), 274 nm for poly(**2a**), 350 nm for poly(**2b**), 281 nm for poly(**4b**), concentrations: poly(**1b**): 5.8×10^{-5} M, poly(**2a**): 4.8×10^{-5} M, poly(**2b**): 2.4×10^{-5} M, poly(**4b**): 2.4×10^{-5} M).

On the other hand, the fluorescence spectra of the polymers varied largely, depending on the substituents (Fig. 3). This suggests that vibrational relaxation is different from polymer to polymer. However, no solvatochromism was observed in the UV–vis and fluorescence spectra of poly(**1b**) measured in THF, toluene, and 1,4-dioxane.

3.5. Electrochromism of polymers

Fig. 4 depicts the UV–vis spectra of voltage-applied poly(**1b**) and poly(**2b**) films. The films were fabricated by spin coating on ITO glass. The absorption maxima appeared around 700 nm by applying voltages higher than 900 mV, especially in poly(**1b**). This is
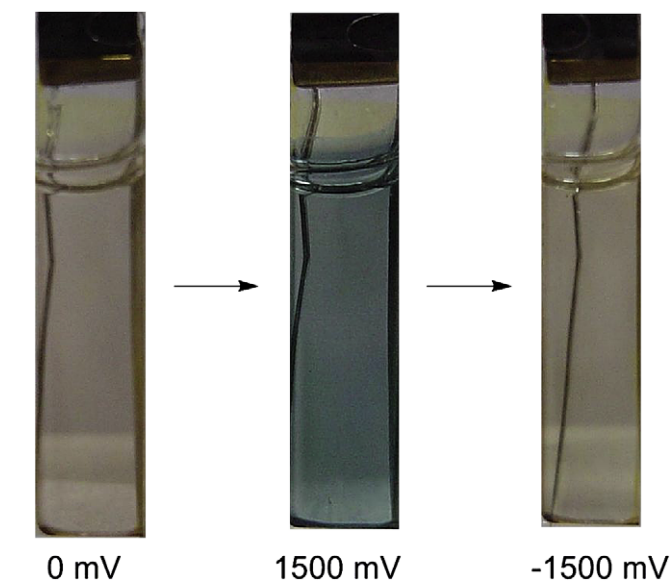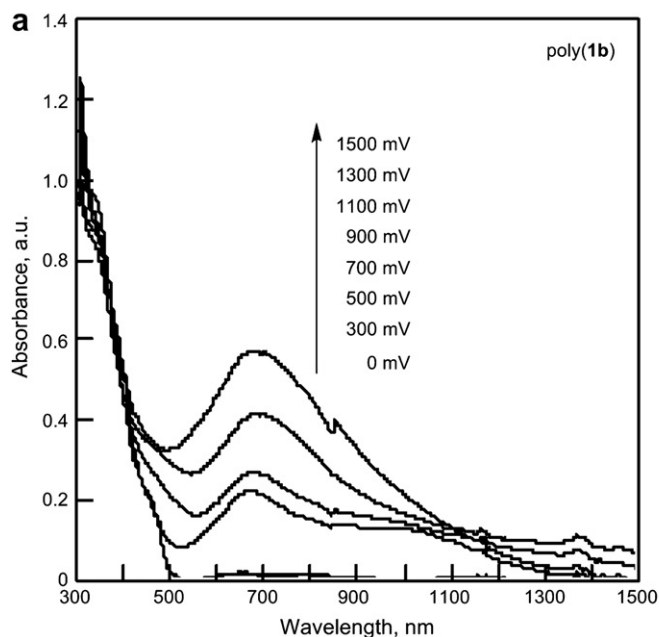

Fig. 5. Images of the ITO electrode coated with poly(**1b**) under application of 0 mV, 1500 mV, and −1500 mV.

attributed to the generation of a low energy level due to the formation of charged polaron at the triphenylamine moiety. The polymer films were yellow-colored before the application of electric potential, while they turned blue by applying a voltage of 1500 mV. Furthermore, the films regained the original yellow color when a negative voltage of −1500 mV was employed (Fig. 5, for interpretation of the references to color in text, the reader is referred to the web version of this article). However, the poly[*p*-(trimethylsilyl)diphenylacetylene] film did not display electrochromism thus suggesting the significance of amino group to endow the polymers with electrochromism.

3.6. Cyclic voltammograms of polymers

The cyclic voltammograms of poly(**1b**), poly(**2a**), and poly(**2b**) were measured, and results are shown in Fig. 6. The intensity of the
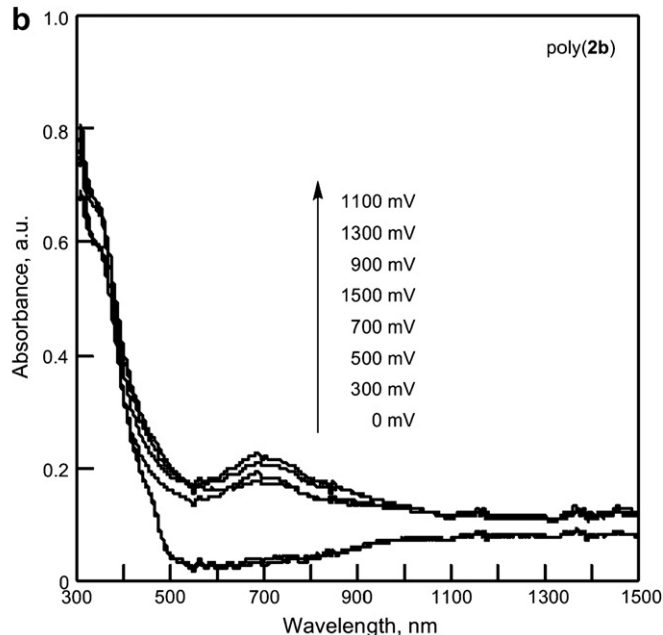

Fig. 4. UV–vis spectra of poly(**1b**) and poly(**2b**) films under application of voltage.
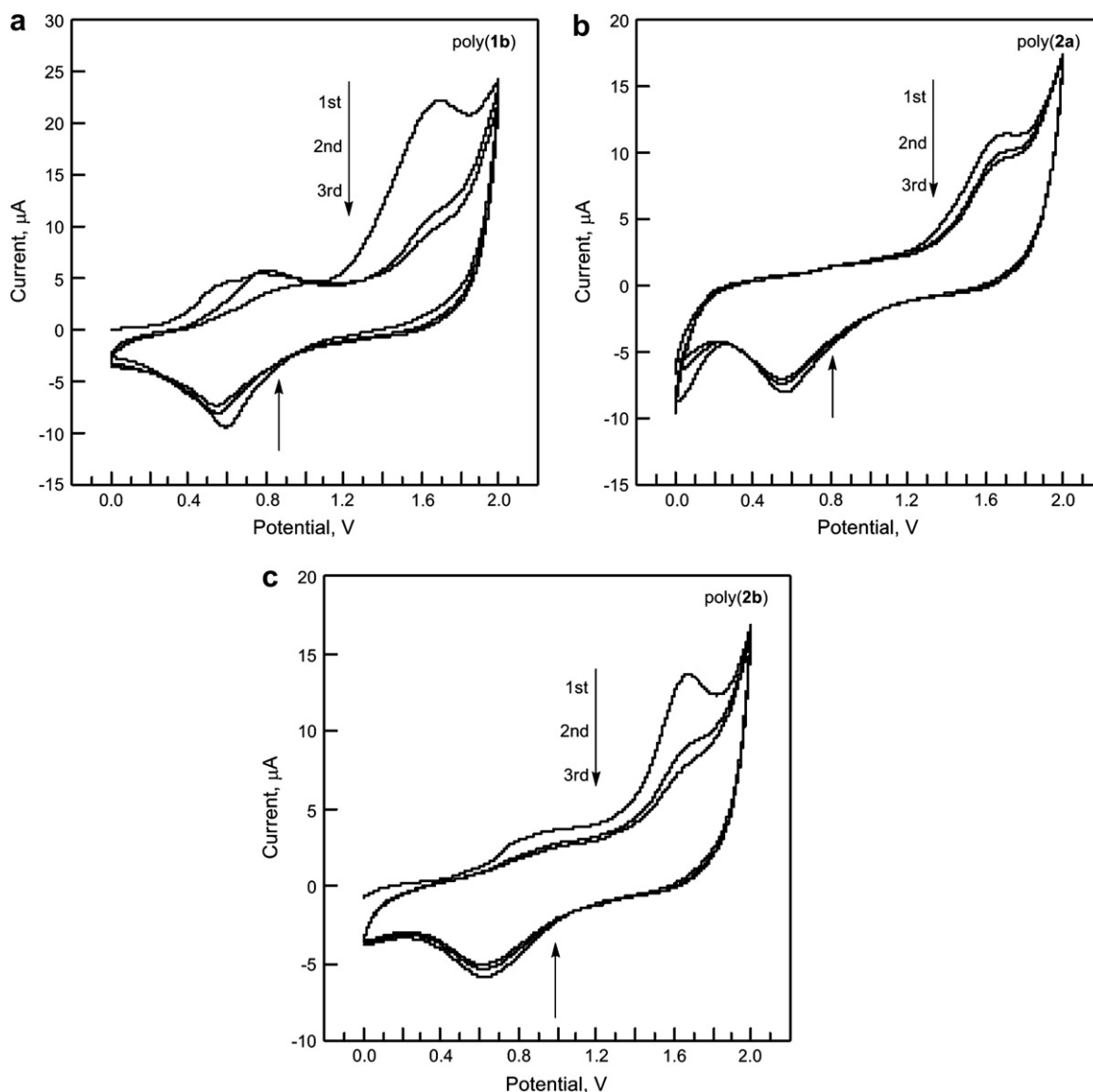
Fig. 6. Cyclic voltammograms of poly(**1b**), poly(**2a**), and poly(**2b**) (1.0 mM) measured in CH_2Cl_2 solution in the presence of TBAP (tetrabutylammonium perchlorate) (0.10 M) with consecutive scans at 0.1 V/s.

oxidation and reduction peaks decreased with the scan time of measurement. This might be due to the formation of thin films of polymers on the surface of the electrode. The redox reaction of poly(**2a**) possessing carbazole moieties did not change very much with scan time as those of poly(**1b**) and poly(**2b**) having triphenylamine moieties. The reduction peaks of poly(**2a**) did not increase, indicating that the dimerization at 3- or 6-position of carbazole did not occur.

4. Conclusion

This paper has revealed that some of diphenylacetylenes bearing tertiary amine moieties, such as diphenylamine, carbazole, and indole, polymerize with tantalum catalyst system. This is the first example of polymerization of diphenylacetylenes having triphenylamine and indole moieties. The monomer with cyclohexylphenylamine substituent, having high electron density on the nitrogen atom, could not polymerize indicating that the polymerizability is largely affected by the electron density on the nitrogen atom. A few of the present series of polymers could be fabricated into free-standing membranes and poly(**2f**) and poly(**4b**) exhibited

good CO_2 separation performance, owing to the affinity of polar amine groups for carbon dioxide. Some polymers displayed absorption maxima around 700 nm in UV–vis spectra by applying voltage, which is explained by the formation of low energy-level excited states of radical cations.

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