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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_4Sn (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.

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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]. Unsubsituted 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*-$BuMe_2Si$ 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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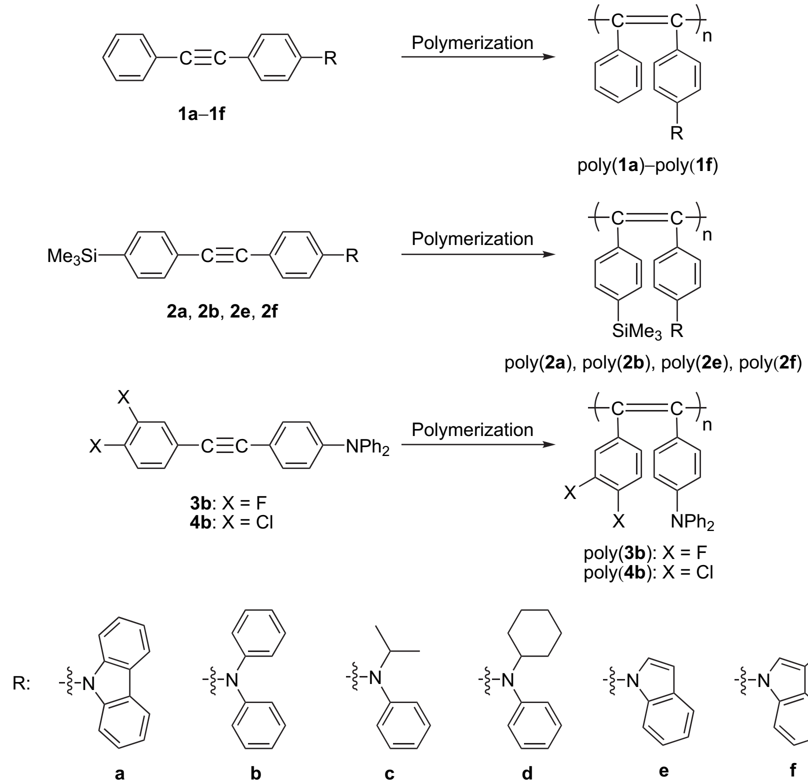

Scheme 1. Polymerization of monomers **1–4**.

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 ($CHCl_3$ 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. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in $CDCl_3$ on a JEOL EX-400 spectrometer. Chemical shifts (δ) for ^1H 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 CH_2Cl_2. UV–vis spectra of polymer films under application of voltage were measured as follows. A polymer solution (0.2 M in $CHCl_3$) 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

$TaCl_5$ (Strem) as catalyst was used as received, while *n*-Bu_4Sn (Wako) as cocatalyst was purified by distillation before using. Phenylacetylene (Aldrich), triphenylamine (Aldrich), triethylamine (Wako), triphenylphosphine (Wako), copper iodide (Wako), Pd_2(dibenzylideneacetone)$_3$ ($Pd_2(dba)_3$, 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),

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