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Oxygen Permeability Change of Polyphenylacetylene Derivatives by Postfunctional TCNE Addition

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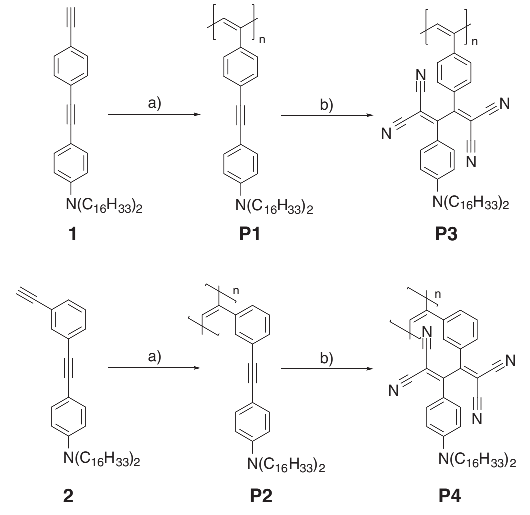
Polyphenylacetylene derivatives substituted by dialkylanilino-appended alkyne side chains were synthesized by Rh-catalyzed polymerization. Improved oxygen barrier ability was achieved by the postfunctional, controlled introduction of four nitrile groups into the repeat unit of the polyphenylacetylene derivatives.

Nitrile polymers have been of significant interest as gas barrier membranes due to the dipole-induced self-assembling characteristics.[1] Polyacrylonitrile (PAN) is the simplest nitrile polymer structure and has been employed as a commercial material. However, since the homopolymer has low solubilities in common organic solvents, the copolymerization of acrylonitrile with other vinyl monomers is usually required to provide good solubilities and processabilities. The polymer structure–gas transport property relationship, i.e., effects of the nitrile content on the gas transport properties, has been investigated.[2] However, it is generally difficult to perfectly reproduce the nitrile content of the copolymers by radical copolymerization on a small laboratory scale.

We recently established a new method for introducing nitrile-based acceptor moieties into alkyne-substituted polymers. This method is based on a postfunctional modification using high-yielding thermal additions between the electron-rich alkynes and small acceptor molecules, such as tetracyanoethylene (TCNE).[3] The alkynes activated by electron-donating groups (EDGs) undergo a [2 + 2] cycloaddition with the electron-deficient ethene moiety of TCNE to form a cyclobutene intermediate, followed by ring opening to yield a chemically stable tetracyanated product (Scheme S1).[4,10] When aromatic amino groups are employed as an EDG, the addition reaction quantitatively proceeds under mild conditions, resulting in a dramatic change in the polymer properties. For example, the Frontier energy levels of p-type semiconducting polymers were gradually reduced as more TCNE was added.[5] This result suggested that the nitrile amounts in a polymer can be strictly controlled by this postfunctionalization method. Furthermore, the solubility and film formation capability are also tuned by the design of the precursor polymer structures.

In order to estimate the effect of this method on improving the gas barrier properties, we selected polyphenylacetylene as the precursor polymer. Since polyacetylene derivatives are generally known to be high gas permeable materials, a clear change in the gas permeability is expected after the postfunctionalization.[6] We now report for the first time the postfunctional control of the oxygen permeability using soluble polyphenylacetylene derivatives.

Phenylacetylene derivatives **1** and **2**, prepared according to our previous report,[3c] were employed as monomers. It should be noted that these monomers possess both terminal and internal alkynes. However, only the terminal alkynes were selectively polymerized in the presence of $[Rh(nbd)Cl]_2$ (nbd: 2,5-norbornadiene) as the catalyst and triethylamine as the cocatalyst, keeping the internal alkynes inert under these conditions.[7] The polymerization was performed in toluene at 20 °C for 24 h, yielding dark yellow polymers. It was found that the catalyst amount is the key factor for achieving the high molecular weight polymers in high yields. Thus, the polymerization of **1** in the presence of the 0.5 mol % Rh catalyst provided the corresponding polyphenylacetylene derivative **P1** with the M_n of 54000 and M_w/M_n of 3.03 in 24% yield, while an increase in the catalyst to 5 mol % yielded **P1** with the M_n of 66300 and M_w/M_n of 3.06 in 72% yield (Scheme 1). Similar to **P1**, **P2** with the M_n of 90500 and M_w/M_n of 2.91 was obtained from **2** in a yield of 70%. The chemical structures of **P1** and **P2** were confirmed by their ^{1}H NMR and IR spectra. In the ^{1}H NMR spectra, the characteristic peak of the terminal alkynes centered at 3.19 ppm disappeared, while the aromatic proton peaks became broader due to the polymer effect (Figure S1[10]). The IR spectra displayed the weak, but well-defined peak ascribed to the side chain alkyne vibration at 2209 cm^{-1} for **P1** and 2208 cm^{-1} for **P2** (Figure S2[10]). Moreover, both polymers showed good solubilities in common organic solvents, such as toluene,



Scheme 1. Synthesis of polyphenylacetylene derivatives: (a) $[Rh(nbd)Cl]_2$, triethylamine, toluene, Ar, 20 °C, 24 h; (b) TCNE, *o*-dichlorobenzene, N_2, 100 °C, 24 h.

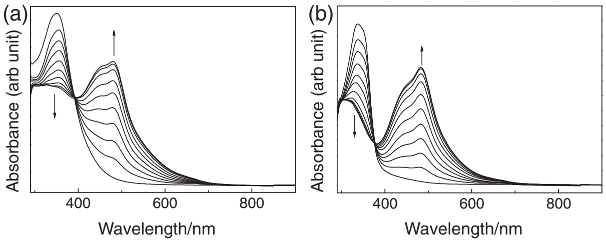


Figure 1. UV–vis spectral changes of (a) **P1** and (b) **P2** upon titration with TCNE (0–1.0 equiv) in *o*-dichlorobenzene at 100 °C.

tetrahydrofuran, chloroform, and dichloromethane, due to the long hexadecyl chains.

Subsequently, the postfunctionalization of these polymers using the TCNE addition to the dialkylanilino-substituted alkynes was attempted. To estimate the reactivity, titration experiments of **P1** and **P2** with a TCNE solution were performed and the UV–vis spectral changes were monitored (Figure 1). The original absorption spectra of **P1** and **P2** in *o*-dichlorobenzene indicated the longest wavelength absorption maximum ($\lambda_{\max}$) at 350 and 337.5 nm, respectively. **P1** with the *p*-phenylene linker between the polyacetylene main chain and the side chain moieties displayed a bathochromically shifted absorption compared to **P2** with the *m*-phenylene linker. Upon the stepwise addition of a TCNE solution at 100 °C, a new charge-transfer (CT) band appeared at 479 nm for **P1** → **P3** and at 482 nm for **P2** → **P4**, and the intensities slowly increased. The increase in the CT band intensity saturated after 60 min at 100 °C until the stoichiometric amount of TCNE was added. The presence of the isosbestic point at 392 nm for **P1** → **P3** and at 376 nm for **P2** → **P4** indicated that no side reactions occurred. It is interesting to note that the CT band positions of **P3** and **P4** are almost the same, despite the different connectivities (vide supra). This result suggested that the π conjugation between the polyacetylene main chain and side chain chromophores is almost disrupted even for **P3**. In contrast to the previous smooth postfunctionalization of side chain alkynes performed under mild conditions,[8] the low reactivity of the TCNE addition was probably due to the steric reason associated with the rigid polymer main chain.

Based on the UV–vis titration experiments, the fully TCNE-adducted polymers **P3** and **P4** were prepared by heating the mixed solution of the precursor polymers and TCNE to 100 °C, followed by evaporation of the solvents. Because no further purification is required, using this postfunctionalization is a great advantage. GPC measurements of **P3** and **P4** revealed an increase in the molecular weights compared to those of the corresponding precursor polymers (Table 1). Furthermore, the polydispersities slightly increased after the postfunctionalization. These changes were more significant for **P1** → **P3** than for **P2** → **P4**, suggesting that **P2** with the *m*-phenylene linker originally has a larger hydrodynamic volume in the GPC measurements. The ^{1}H NMR spectra of **P3** and **P4** displayed broader peaks in the aromatic region, indicating the increased rotational barriers of the single bonds due to the bulky and nonplanar 1,1,4,4-tetracyanobutadiene (TCBD) moieties (Figure S1[10]). In the IR spectra, a weak vibrational peak at 2208–2209 cm^{-1} ascribed to the internal alkynes of the precursor polymers was replaced by a strong nitrile peak at 2214 cm^{-1} for the TCNE-adducted polymers (Figure S2[10]). The elemental analyses of **P3** and **P4** were in good agreement with the calculated values. All these results supported the perfect postfunctionalization by the alkyne–TCNE addition reaction.

Table 1. Summary of molecular weights and thermal properties of the polymers

Polymer	M_n[a]	M_w/M_n[a]	$T_{d5\%}$/°C[b]
P1	66300	3.06	384
P2	90500	2.91	394
P3	210000	4.01	334
P4	159600	3.41	330

[a]Molecular weight determined by GPC (eluent: THF, calibrated by standard polystyrenes). [b]The 5% weight-loss temperature determined by TGA at the heating rate of 10 °C min^{-1}.

High thermal stability is an important factor for practical applications. To reveal the thermal properties of the polyphenylacetylene derivatives, thermogravimetric analysis (TGA) was performed at the heating rate of 10 °C min^{-1} under flowing nitrogen. Although the precursor polymers **P1** and **P2** showed a single-step decomposition with the 5% decomposition temperatures ($T_{d5\%}$) of 384 and 394 °C, respectively, the postfunctionalized polymers **P3** and **P4** displayed a two-step decomposition with the onset decomposition temperatures being ca. 330 °C (Figure S3[10] and Table 1). The newly introduced nitrile groups were probably associated with the first decomposition step, but the postfunctionalized polymers retained sufficient thermal stabilities.

The postfunctionalization was also confirmed by the optical and electrochemical data. The optical band gaps of **P1** and **P2** calculated from the end absorption (λ_{end}) in *o*-dichlorobenzene were 2.84 and 3.25 eV, respectively, while the λ_{end} values of **P3** and **P4** reached into the near-infrared with the optical band gap of ca. 1.6 eV (Table S1[10]). After the postfunctionalization, the polymer band gaps became almost the same. The electrochemical band gaps were determined using differential pulse voltammetry (DPV) in CH_2Cl_2 with 0.1 M $(n\text{-}C_4H_9)_4NClO_4$ at 20 °C, because the cyclic voltammogram (CV) under the same conditions did not provide clear peaks of both the oxidation and reduction. The precursor polymers **P1** and **P2** displayed the first oxidation wave ($E_{\text{ox},1}$) ascribed to the dialkylanilino moieties at almost the same potential of 0.39 and 0.42 V (vs. Fc^+/Fc), respectively (Table S1 and Figure S4).[10] This result suggests the negligible electrostatic interactions between the side-chain pendants. The $E_{\text{ox},1}$ values of the TCNE-adducted **P3** and **P4** anodically shifted to 0.83 and 0.85 V, respectively, due to the intramolecular interaction with the electron-withdrawing TCBD moiety. Additionally, **P3** and **P4** exhibited the TCBD-centered first reduction wave ($E_{\text{red},1}$) at −1.08 and −1.03 V, respectively. The calculated electrochemical band gaps of **P3** and **P4** were almost the same (ca. 1.9 V), implying that these band gaps mainly originate from the side-chain chromophores.

Polymer membranes were prepared by casting 2 mL of the toluene solutions at a concentration of 20 g L^{-1} onto a Teflon boat, followed by slow evaporation of the solvent at 20 °C. **P1**, **P3**, and **P4** provided tough films sufficient for the oxygen permeability measurements, while the **P2** film was too fragile. The oxygen permeability coefficients (P_{O_2}) were measured at 30 °C. The P_{O_2} of the precursor polymer **P1** was 20 barrers, which is a reasonable value based on previous systematic investigations of substituted polyacetylene derivatives.[6] This permeability clearly decreased when nitrile groups were intro-

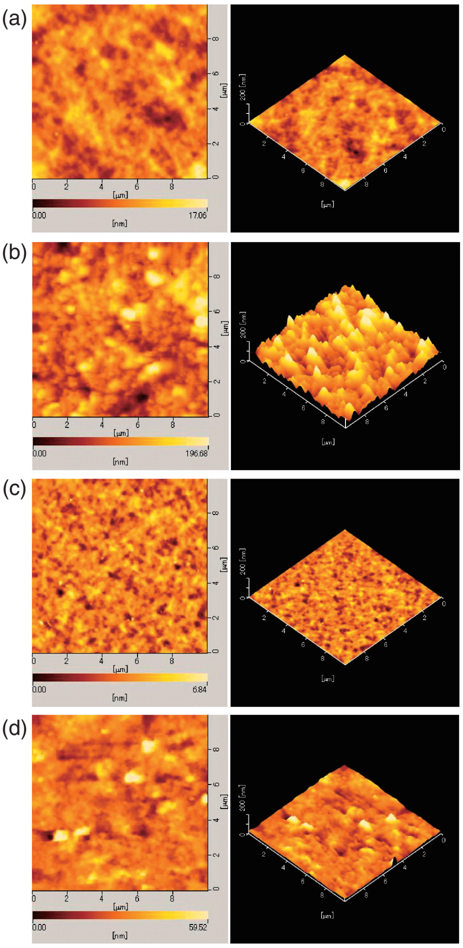


Figure 2. AFM images ($10 \times 10\,\mu m^2$) of the cast films of (a) **P1**, (b) **P3**, (c) **P2**, and (d) **P4**.

duced by the postfunctionalization reaction. Thus, the P_{O_2} of the TCNE-adducted polymer **P3** was 6.1 barrers, which is approximately 30% of that of the precursor polymer. In other words, the oxygen barrier property was enhanced by 3.3 times due to this postfunctionalization. The P_{O_2} of **P4** with the different connectivity mode was 18 barrers, suggesting the presence of more voids in the polymer film than in the **P3** film. In order to reveal the surface morphology, the polymer membranes were analyzed by atomic force microscopy (AFM). The AFM images of the precursor polymers **P1** and **P2** exhibited very smooth surfaces with the roughness parameter (RMS) values of 2.05 and 0.12 nm, respectively (Figures 2a and 2c). On the other hand, the surfaces of the postfunctionalized polymers **P3** and **P4** showed aggregated particles with a diameter of 100–200 nm (Figures 2b and 2d). The driving force of the aggregate formation was probably based on the intermolecular interactions between the nitrile groups. Consequently, the RMS values of **P3** and **P4** dramatically increased to 30.76 and 7.36 nm, respectively. **P3** with the *p*-phenylene linker appears to possess better intermolecular interactions than **P4** with the *m*-phenylene linker. This idea was indeed supported by the measured P_{O_2} values.

There are, to the best of our knowledge, several reports that describe the gas permeability change by the postfunctionalization of polymer films. For example, Masuda et al. reported the reduced gas permeability or enhanced gas barrier property of insoluble polyphenylacetylene membranes by removal of the silyl protecting groups.[9] After the deprotection of the silyl substituents, the resulting hydroxy groups contributed to the increased gas barrier performance in terms of hydrogen bonds, although no surface morphology was investigated. In contrast, there are no suitable protecting groups for the nitrile functionality. Therefore, the clean postfunctionalization based on the high-yielding alkyne-TCNE addition is the only promising method for controlling the intermolecular interactions and concomitant gas permeabilities.

In summary, we have demonstrated the successful introduction of nitrile groups into high molecular weight polyphenylacetylene derivatives with high thermal and chemical stabilities. Intermolecular dipolar or multipolar interactions between the nitrile moieties lead to the formation of 100 nm-sized polymer aggregates and possibly reduced the free volume in the polymer membranes. These morphology changes resulted in the decreased oxygen permeability. Different connectivities, such as the *p*- and *m*-phenylene linkers, mainly affected the film formation capability. **P3** with the *p*-phenylene linker displayed the better film formation and oxygen barrier performance than **P4** with the *m*-phenylene linker. The effects of other chemical structures, such as conjugated main chain and alkyl chain length, are to be elucidated. Also, the permeability measurements of various gases are important in order to achieve a high selectivity of a specific gas. These studies are currently underway in our laboratory.

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