【別紙２】

論文名：Permselective membranes from imine-containing cis-cisoidal polyacetylenes using imine exchange reactions（要約）

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（以下要約を記入する）

We have already reported that tightly helical polyphenyl- acetylenes having many hydroxy groups (poly(RDHPA))[1] showed good oxygen permselectivity (α)[2,3] and highly selective photoaromatic cyclization (SCAT)[4] to poly(RDHPA) enhanced their α.[2] Ladder[5] and multi-bridged[6] structures were suitable for improving their α. *Soluble* 2D network polymer membranes with angstrom-sized pores and thicknesses have not been reported. Herein, novel *soluble* 2D macromolecular sheets with angstrom-sized pores (24.6 angstrom) and thickness (3.4 angstrom) are synthesized by solid-solid interface polycondensation in laminated membranes of two cis-cisoid poly(imino-containing phenylacetylene)s followed by highly selective photocyclic aromatization (SCAT) (Fig.1). First, a two-layered laminated polymer membrane that is self-supporting is prepared and solid-solid interfacial polycondensation performed (Sche.2). The *insoluble* three-dimensional (3D) network polymer layer formed is isolated by removing the soluble unreacted polymer layers. Finally, a SCAT reaction is carried out by irradiation of visible light on the *insoluble* 3D membrane to produce a *soluble* 2D macromolecular sheet. The precise 2D molecular structure is obtained, such as the degree of polymerization, thickness, fraction of rings (pores), and pore size, which can be estimated by GPC, AFM, ^{1}H-NMR, IR, and XRD, because the macromolecule is *soluble*. Composite membranes containing the 2D macromolecular sheet show good oxygen permselectivity exceeding the Robeson upper line, possibly because the angstrom-sized pores and thicknesses produce high oxygen permselectivity without suppressing the permeability (Fig.2).

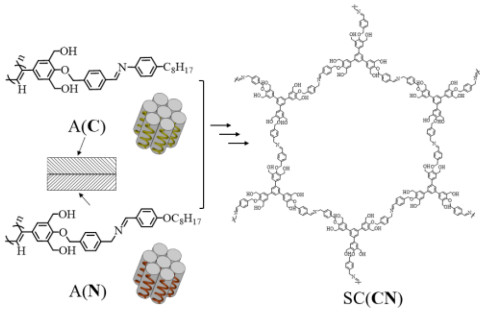
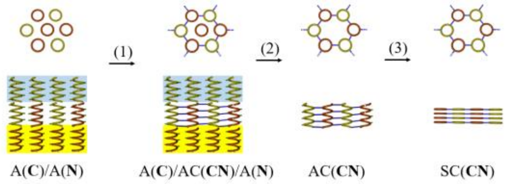


Figure 1. Chemical structure of two-dimensional (2D) macromolecular sheet.



Scheme 1. Synthetic route to two-dimensional (2D) macromolecular sheet (SC(**CN**)) by solid-solid interfacial polycondensation (1) between A(**N**) and A(**C**) in its laminated membrane (A(**C**)/A(**N**)) followed by a SCAT reaction (3) of the resulting *thin* network polymer membrane (AC(**CN**)).

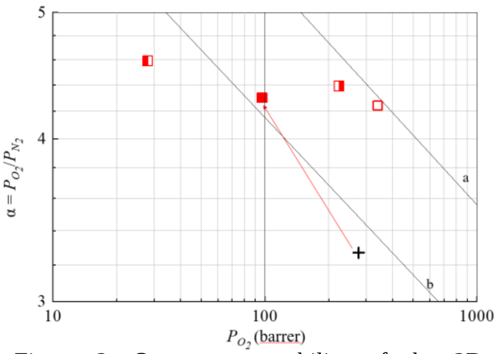


Figure 2. Oxygen permeability of the 2D macromolecular sheets. +: for A(**C**)/A(**N**); ■: for A(**C**)/AC(**CN**)/A(**N**); ◧ : for AC(**CN**) from A(**C**)/AC(**CN**)/A(**N**); ◨ : for AC(**CN**) from AC(**CN**)/PDMS; □: for SC(**CN**) from SC(**CN**) /PDMS. (a and b indicate Robeson's boundary lines in 2008 and 1991, respectively.)

References: T. Aoki et al.: 1. *J. Am. Chem. Soc.*, **125**, 6346 (2003). 2. *Polymer*, **149**, 117 (2018). 3. *Chem. Lett.*, **47**, 1314 (2018). 4. *J. Am. Chem. Soc.*, **135**, 602 (2013). 5. *Chem. Lett.*, **45**, 424 (2016). 6. *Chem. Lett.*, **46**, 401 (2017).