

論文名 : Synthesis and reaction of polyphenylacetylenes having N-imines in the pendant groups and permeation of the resulting polymer membranes
(要約)

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In Chapter 1, new types of multi-bridged copolymers were designed and examined as an oxygen permselective membrane material. The multi-bridged copolymers were synthesized by imine metathesis reactions between N-imines(synthetic equivalent of amines)-containing poly(substituted acetylene)s and C-imines(synthetic equivalent of aldehydes)-containing poly(substituted acetylene)s in the membrane state. The resulting copolymers maintained good self-membrane forming ability. The introduction of multi-bridge structures enhanced both oxygen permselectivities and oxygen permeabilities simultaneously.

In Chapter 2, in the case of the metathesis reaction of the mixture of poly(1) and poly(2) in the membrane state, the resulting polymers, copoly (poly(1) / poly(2))s were partly insoluble, therefore, no GPC and NMR data of the main part were obtained. In order to obtain more information of the molecular structures of copoly (poly(1) / poly(2))s, we carried out the metathesis reaction of the mixture of poly(1) and poly(2) in solution. The resulting copoly (poly(1) / poly(2))s were totally soluble and therefore we could measure their GPC and NMR. Oxygen permeability behaviours of membranes from copolymers synthesized by imine metathesis in different conditions and together with their precursor homopolymer or blend membrane before metathesis reaction were discussed.

In Chapter 3, seven novel phenylacetylene monomers(1-7) having two imine, amine or secondary amine groups were synthesized and polymerized by using $[\text{Rh}(\text{nbd})\text{Cl}]_2$ as a catalyst. The resulting polymers showed different solubility, membrane forming ability and oxygen permselectivities. The solubility characteristics of the polymers (1, 2, 4, 5, 6) bearing protected amino groups were quite different from those of the unprotected ones(3), the former being soluble in apolar solvents, whereas the latter displayed poor solubility even in polar solvents. Freestanding membrane fabrication by solution casting were successful for poly(1), poly(2), poly(4) and poly(7), oxygen permeability (PO_2) and permselectivity ($\alpha=\text{PO}_2/\text{PN}_2$) was discerned in comparison with the different kind of amine groups. N-imine in poly(1) showed higher PO_2 and α than the other N-imine in poly(2), the higher PO_2 is caused by the higher

polarity of phenolic hydroxyl groups which can interact with O₂ and improve the PO₂. The poly(1) membrane more flexible than poly(2), its maximum flexural stress is higher than poly(2), the fewer defects enhanced the α . After the imine bonds were reduced to secondary amine bonds, the bonds could rotate freely, the polymer became more flexible than poly(1), the PO₂ increased, the DO₂ and DO₂/DN₂ decrease caused the α to decrease. Poly(7) showed low PO₂ and α , may be because the polymer without purification.

In Chapter 4, three new phenylacetylene monomers(1-3) having three substituents including one or two carbamate groups were synthesized and polymerized by using [Rh(nbd)Cl]₂ as a catalyst. The resulting polymers had very high molecular weights of 1.4 - 4.8×10⁶ with different solubility and membrane forming ability. By introducing two carbamate groups, the solubility and membrane forming ability of polyacetylene poly(3) were enhanced highly. The oxygen permeability coefficients of poly(3) membrane (PO₂= 420) were more than 135 times higher than that of polymer having no carbamate group (PO₂=3.09 for poly(DoDHPA)) with only a small drop in oxygen permselectivity (α =PO₂/ PN₂). These properties were affected by the difference of conformation and polarity of the resulting polymers. By introducing two carbamate groups into the phenylacetylene monomer (3), the resulting polymer main chains consisted of more extended and flexible cis-transoid conformations and the polarity was low, they were flexible enough for forming a self-standing membrane and enhance the oxygen permeability. On the other hand, the polymers having two hydroxy groups and a carbamate group(poly(1) and poly(2)), had very tight cis-cisoid conformations maintained by intramolecular hydrogen bonds and the polarity was high. They caused the low solubility, membrane forming ability and oxygen permselectivity compared with poly(3).