らせん置換アセチレンポリマーの環化芳香族化光分解を利用した各種光学分割膜の調製と光学異性体選択透過

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Preparation and enantioselective permeation of several membranes prepared using highly selective photocyclic aromatization of helical polyacetylenes

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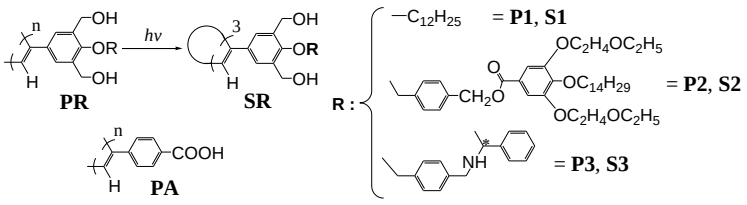
We previously reported helical **P1** were quantitatively decomposed to their corresponding cyclic trimers (**S1**) by visible light irradiation (SCAT). In this presentation, we prepared the following three kinds of optical resolution membranes by using the SCAT reaction. **I**) chiral supramolecular polymer membranes from one-handed helical chiral polymers, **II**) chiral channel polymer membranes prepared by CPL SCAT of racemic helical polymer membranes, and **III**) chiral channel polymer membranes prepared by selective SCAT reaction of blend membranes consisting of SCAT-active chiral helical template polymers and SCAT-inactive achiral helical matrix polymers.

Keywords : Helical poly(substituted acetylene)s; Highly selective photocyclic aromatization; Optical resolution membrane; Enantioselective permeation

[序論] 当研究室では以前 **P1** の高選択光環化分解反応(SCAT)を報告した(Scheme 1)。[1] 本発表では SCAT を利用した以下の 3 つの膜(Scheme 2, **I**, **II**, and **III**)の光学異性体選択透過を述べる。**I**) SCAT によるキラル超分子ポリマー膜[2]、**II**) 偏光 SCAT によるキラルチャネルポリマー膜。**III**)選択的 SCAT で得られたキラルチャネルポリマー膜。[3]

[結果と考察] いずれの膜もフェネチルアルコールラセミ体メタノール溶液の透過において、光学異性体選択透過性を示した(図 1; **I** 膜:87.4%ee, **II** 膜: 8.8%ee, **III** 膜: 10.2%ee)。3 つの膜の中では、**I** 膜が最も優れた性能を示した。



Scheme 1. SCAT of cis-cis polyacetylenes (**PR**) to the corresponding cyclic trimer (**SR**).

I. (+)-**P2** $\xrightarrow{1)\ h\nu}$ (+)-**S2** or (-)-**P2** $\xrightarrow{1)\ h\nu}$ (-)-**S2**

II. (+)-**P1** / (-)-**P1** $\xrightarrow{1)\ \text{R-CPL}}$ (+)-**S1** / (-)-**P1** $\xrightarrow{2)}$ chiral pores / (-)-**P1**

III. (R)-**P3** / **PA** $\xrightarrow{1)\ h\nu}$ (R)-**S3** / **PA** $\xrightarrow{2)}$ chiral pores / **PA**

Scheme 2. Preparation of membranes **I**, **II**, and **III** for enantioselective permeation. 1) SCAT, 2) removal of **SR**.

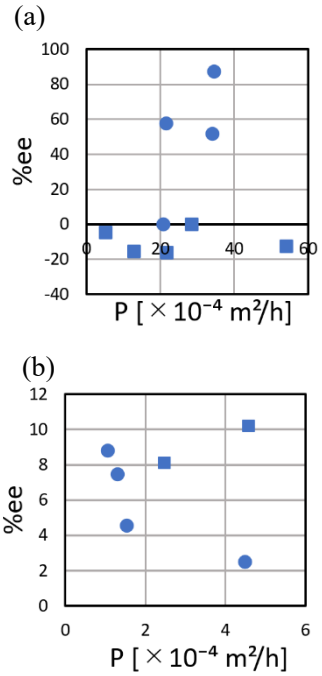


Fig. 1. Enantioselective permeation of racemic 1-phenylethyl alcohol in methanol through membranes. (a) **I** (●: (+)-**S2**, ■:(-)-**S2**); (b)**II**(●), **III**(■).

1) T. Aoki *et al.*, *J. Am. Chem. Soc.*, **135**, 602 (2013). 2) T. Aoki *et al.*, *Macromol. Chem. Phys.*, **216**, 530 (2015). 3) 青木ら，日本化学会第 100 春季年会 3C2-19(2020).