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Enantioselective Pervaporation through Membranes from Poly(1,3-phenyleneethynylene)-based One-handed Helical Foldamer and Unfoldamer

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We synthesized two kinds of poly(1,3-phenyleneethynylenes), one has (+)-menthoxycarbonyl groups at all repeating units and the other has (+)-menthoxycarbonyl groups and *n*-dodecyloxy groups alternately. Self-supporting membranes could be obtained easily by solvent casting. Enantioselective permeations of the polymers were investigated by pervaporation of 2-butanol. Enantioselective permeabilities of the membrane consisting of one-handed helical foldamer and unfoldamer were clarified.

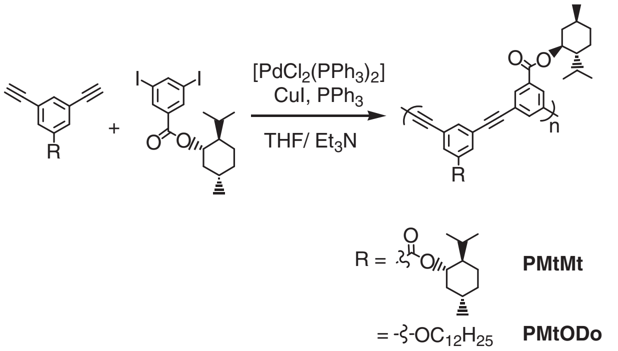
Syntheses of optically active helical polymers have attracted particular interests of polymer scientists due to interesting technological applications in optical resolution, chiral sensors, chiroptics, microelectronics, chiral magnets, and so on.[1]

It is well known that some poly(1,3-phenyleneethynylene)s can form helical foldamer conformation depending on their side groups and/or solvent.[2–6] These properties are very interesting and many functions such as molecular recognition,[7–10] magnetism,[11,12] and reactive sieve[13] have been reported.

However, to the best of our knowledge, functions of poly(1,3-phenyleneethynylenes) used as free-standing membrane have been never reported.[14] Needless to say, there are no reports that functions of free-standing membranes consisting of foldamer and unfoldamer were compared. Enantioselective permeation by chiral main chains of polymers is a very interesting subject in polymer science. Herein, we synthesized two kinds of chiral poly(1,3-phenyleneethynylenes), one has (+)-menthoxycarbonyl groups at all repeating units and the other has (+)-menthoxycarbonyl groups and *n*-dodecyloxy groups alternately in the repeating units (named **PMtMt** and **PMtODo**, respectively) (Scheme 1). Then we prepared free-standing membranes consisting of one-handed helical foldamer and unfoldamer by casting and investigated the enantioselective permeability of the foldamer and the unfoldamer membranes.

PMtMt was synthesized according to a previous report from our laboratory.[15] **PMtODo** was newly synthesized to improve solubility and membrane forming ability.[16] The polymerization data for the polymers used in this paper are summarized in Table 1. Both polymers were pale yellow solids and soluble in chloroform, dichloromethane, carbon tetrachloride, THF, toluene, and benzene and insoluble in hexane, diethyl ether, methanol, and acetone.

PMtODo in toluene displayed intense Cotton effects in circular dichroism (CD) spectra in the range of 270–360 nm which are attributable to the backbone. This indicates that **PMtODo** in toluene forms one-handed helical foldamer. On the other hand, no Cotton effects were observed in chloroform solution because **PMtODo** exists in extended chain conformation (unfoldamer) in chloroform.



Scheme 1. Synthesis of chiral poly(1,3-phenyleneethynylenes).

Table 1. Polycondensation results by using [PdCl$_2$(PPh$_3$)$_2$]–PPh$_3$–CuI (1:4:6)[a]

Code	Yield /%	M_w[b] /$\times 10^4$	M_w/M_n[b]	$[\alpha]_D^{20}$[c] /°	$[\theta]_{320} \times 10^{-3}$[d] /deg·cm^2·dmol^{-1}
PMtMt	72	23.0	2.20	91.0	9.3
PMtODo	50	17.2	1.45	62.0	3.1

[a]Polycondensations were carried out in THF/Et$_3$N for 24 h at r.t.; $[M]_{0,\mathrm{total}} = 0.125$ M, [Pd cat] = 0.025 M. [b]Determined by GPC correlating polystyrene standard; eluent: THF. [c]In CHCl$_3$/benzene (volume ratio: 2:8); 0.10 g L^{-1}. [d]In toluene (2.5×10^{-4} M) at 20 °C.

The CD profile of **PMtODo** in toluene was similar to that of **PMtMt**,[15] but the $[\theta]$ value of **PMtODo** in toluene was one third of that of **PMtMt** in toluene (Table 1). It was attributed to the chiral menthyl group, i.e., menthyl group content of **PMtODo** was less than that of **PMtMt** and less contribution of solvophobic effects by *n*-dodecyloxy groups as a driving force for foldamer formation than that of menthoxycarbonyl groups.

To elucidate a one-handed helical conformation in the membrane state, a thin membrane was prepared on a quartz disc by spin-coating. A strong Cotton effect was observed in the CD spectra of **PMtODo** membrane prepared from toluene solution, which was similar to that of in solution. On the other hand, no Cotton effect was observed in the CD spectra of **PMtODo** membrane prepared from chloroform solution (Figure 1). These results were the same in the case of **PMtMt** previously reported.[15] UV–vis spectra of foldamer and unfoldamer were

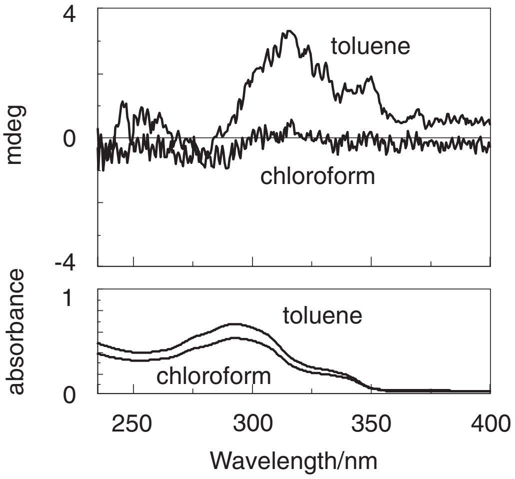


Figure 1. CD and UV–vis spectra of **PMtODo** membrane at 25 °C.

almost the same unlike in solution.[15] It is possible that in membrane the ratio of oscillator strengths for absorption bands of the unfoldamer were similar to that of the foldamer due to an aggregation of the unfoldamer.[5] Since both polymers had a sufficiently high molecular weight, self-supporting membranes can be fabricated by solvent-casting.[17] **PMtODo** gave a more flexible membrane compared with **PMtMt**.

Figures 2 and 3 show the quantity (*Q*) of permeated (*R*)- and (*S*)-2-butanol versus permeation time through foldamer and unfoldamer membranes of **PMtMt** and **PMtODo**, respectively, in pervaporation when racemic 2-butanol was supplied.[18] Using **PMtMt** unfoldamer membrane, (*S*)-isomer preferentially permeated, and the ee of permeate was 89.4% in good selectivity.[17] On the other hand, using **PMtMt** foldamer membrane, permeateselectivity was hardly observed.

In contrast with these results, using **PMtODo** membranes, unfoldamer membrane scarcely showed enantioselective permeability and foldamer membrane showed a good enantioselective permeability, (*R*)-isomer preferentially permeated, and the ee of permeate was 68.3%.

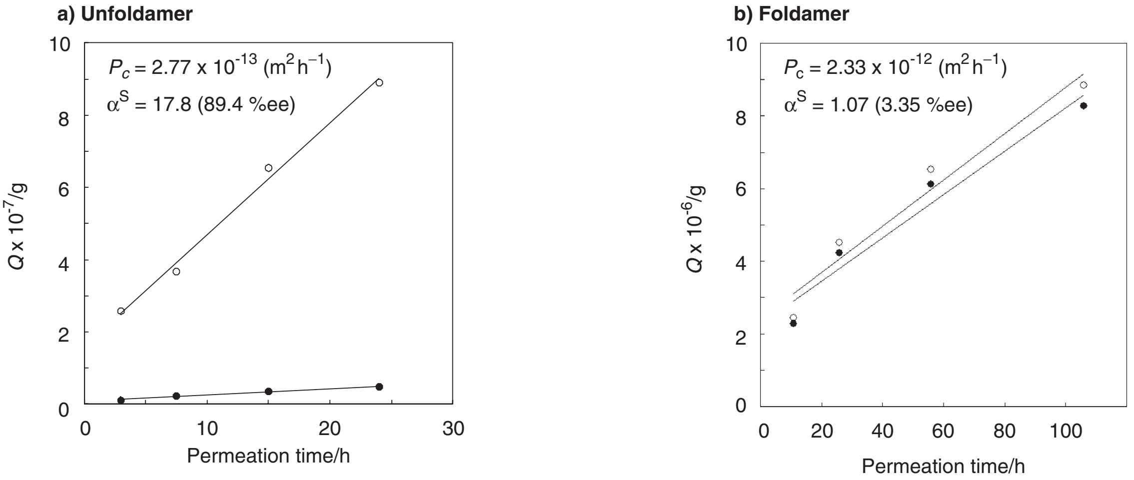


Figure 2. Plots of quantity (*Q*) of permeated (*R*)-(+)-2-butanol (●) and (*S*)-(−)-2-butanol (○) v.s. permeation time through **PMtMt** membrane: a) prepared from chloroform solution (unfoldamer); b) prepared from toluene solution (foldamer).

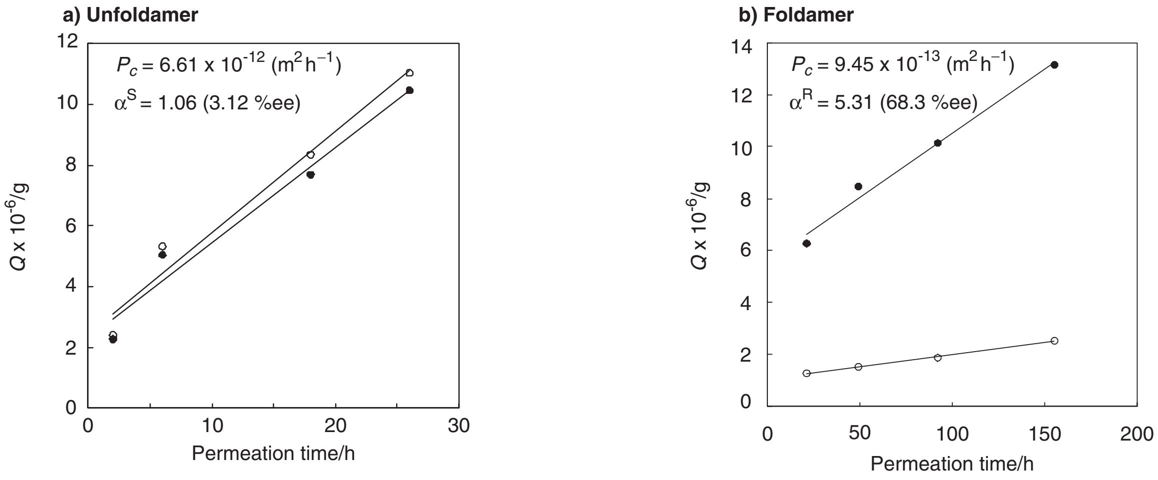


Figure 3. Plots of quantity (*Q*) of permeated (*R*)-(+)-2-butanol (●) and (*S*)-(−)-2-butanol (○) v.s. permeation time through **PMtODo** membrane: a) prepared from chloroform solution (unfoldamer); b) prepared from toluene solution (foldamer).

Quite interestingly, whether foldamer or unfoldamer was a good membrane showing higher selectivity in permeation depended on whether **PMtMt** or **PMtODo** was used. That is, when **PMtMt** membrane was used, the unfoldamer was better. On the other hand, when **PMtODo** membrane was used, the foldamer was better. Furthermore, **PMtMt** unfoldamer membrane and **PMtODo** foldamer membrane showed opposite selectivity. These results indicate a one-handed helical conformation of poly(1,3-phenyleneethynylenes) affected strongly permselectivity. It is possible that the main chain of poly(1,3-phenyleneethynylene) with helical sense inducted by (+)-menthoxycarbonyl groups in side groups interacted preferentially with (*S*)-2-butanol. In contrast, (+)-menthoxycarbonyl groups in side chains themselves maybe interacted preferentially with (*R*)-isomer. Therefore, it is assumed that when the **PMtMt** foldamer membrane was used, both effects unfortunately canceled each other and when the **PMtODo** foldamer membrane was used, the effect of one-handed helical main chain surpassed that of (+)-menthoxycarbonyl groups due to the lower contents of chiral substituents than **PMtMt**. Anyway, a detailed investigation of enantioselective permeation of various chiral poly(1,3-phenyleneethynylenes) is now in progress.

In summry, two kinds of poly(1,3-phenyleneethynylenes) having (+)-menthoxycarobonyl groups in all repeating units (**PMtMt**) and having (+)-menthoxycarobonyl groups and *n*-dodecyloxy groups alternately in the repeating units (**PMtODo**) could be obtained. Fabrication of self-supporting membranes consisting of different conformations, i.e., foldamer (one-handed helical conformation) membrane and unfoldamer membrane was achieved by casting from toluene and chloroform, respectively. It was found that chiral poly(1,3-phenyleneethynylenes) were novel promising materials for optical resolution membranes and the optical resolution ability of chiral poly(1,3-phenyleneethynylenes) was quite different depending on polymer conformation such as unfoldamer and foldamer.

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17 Preparation of a self-supporting membrane: A solution of a polymer in toluene or chloroform (ca. 2–5 × 10^{-2} M based on the monomer unit) was cast on a poly(tetrafluoroethylene) sheet, and the solvent was evaporated for 24 h at room temperature. The resulting solid membrane was detached from the sheet and dried in vacuo for a day. Thickness (L): 30–60 µm, area (A): 8.55 $\mathrm{cm^2}$.
18 Enantioselective pervaporation: The feed side of a stainless steel cell was filled with racemic 2-butanol. The permeate side was connected to a cold trap in dry ice/methanol and evacuated at 0.2 mmHg. Pervaporation was carried out for 30–150 h (t) at 25 °C. The permeate trapped was weighed (Q, g) and the normalized quantity (Q_c, $\mathrm{g\,m\,m^{-2}}$) was calculated from $Q_c = QL/A$. The permeation rate (P, $\mathrm{g\,m\,m^{-2}\,h^{-1}}$) was estimated from the slope of the permeation time (t, h) plot. The permeability coefficient (P_c, $\mathrm{m^2\,h^{-1}}$) was calculated by dividing P by the difference in the concentration between the feed and permeate sides. Enantioselectivity in the permeation, i.e. optical purity of the permeate (%ee), was determined by the equation

$$\%\mathrm{ee} = 100 \times (A_\mathrm{R} - A_\mathrm{S})/(A_\mathrm{R} + A_\mathrm{S})$$

The peak areas of (*R*)- and (*S*)-isomer (A_R and A_S) in the permeate were measured by HPLC with an optical resolution column (CHIRALCELL OD-H manufactured by Daicel Chemical Co.) after carbamoylation of 2-butanol permeate. Carbamoylation of 2-butanol: 2-Butanol permeate was diluted with ether (2 mL). To the solution containing 2-butanol (10 mg, 0.14 mmol) were added pyridine (0.2 mL, 2.5 mmol) and then phenylisocyanate (0.2 mL, 1.8 mmol). The solution was stirred for 3 min at 50 °C, and the solvent was removed. The resulting product was dissolved in hexane, and the solution was used for HPLC measurement.