ORIGINAL ARTICLE

Polymeric pseudo-liquid membranes from poly(dodecyl methacrylate): KCl transport and optical resolution

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A polymeric pseudo-liquid membrane (PPLM) was constructed from poly(dodecyl methacrylate) (PC12MA), which exhibited a rubbery state under membrane transport conditions and was used as the membrane matrix, and from dibenzo-18-crown-6 (DB18C6) or O-allyl-N-(9-anthracenylmethyl)cinchonidinium bromide (AAMC), which was used as a model transporter. Membrane performance was studied using KCl or a racemic mixture of phenylglycine (Phegly) as a model substrate. The PPLM with DB18C6 transported KCl. The membrane transport ability depended on the DB18C6 concentration, implying that DB18C6 worked as a transporter within the PC12MA membrane matrix. L-Phegly was preferentially transported over D-Phegly through the membrane with AAMC from the racemic mixture of Phegly, and the permselectivity was determined to be 1.55. The present results suggest that PPLMs are applicable not only in metal ion transport but also in optical resolution.

INTRODUCTION

Membrane separation is considered to be an environmentally benign separation technology compared with other separation methods.[1–3] Membranes with high permselectivity toward target molecules can be attained by introducing molecular recognition compounds or functional moieties that exhibit molecular recognition toward the target molecule into the membranes. These membranes are divided into two types of membrane system, liquid membranes or solid (polymeric) membranes. The former directly and effectively reflect the affinity of the molecular recognition material (transporter or carrier) that is found in the liquid membrane. Additionally, a liquid membrane is easily constructed by dissolving the transporter in a solvent. However, the drawback of a liquid membrane is its lack of long-term stability; the membrane solution may evaporate or the transporter and/or transporter/target molecule complex may 'wash-out' during operation.[4–9] If these drawbacks can be overcome, a liquid membrane would be a promising membrane system for the separation of a target molecule from a mixture that contains compounds with similar or the same molecular dimensions and compounds that exhibit similar or the same chemical and/or physical properties.

Various studies have obtained durable liquid membranes, including (1) polymer liquid crystal composite membranes,[10,11] (2) polymer inclusion membranes,[12–19] (3) organogel membranes,[20,21] (4) the stabilization of a top layer of supported liquid membranes via interfacial polymerization,[22–24] (5) room temperature ionic liquids,[25,26] and (6) polymeric pseudo-liquid membranes (PPLMs).[27–31] A PPLM is defined as a liquid membrane that consists of polymeric materials in a rubbery state and a transporter for a given target molecule. Polymeric materials in a rubbery state have an important role as a membrane component that dissolves a transporter and as a barrier that separates two phases, such as a source phase and a receiving phase. Because of this setup, a PPLM is different from a supported polymeric liquid membrane,[32–34] which is a microporous hydrophobic membrane, in which the pore is loaded with a polymeric (origomeric) liquid that exhibits an affinity toward the organic compounds of interest. The authors' research group demonstrated that liquid-state polymeric membranes work as a matrix for a liquid membrane.[29–31] The transport mechanism was shown to be a carrier-diffusion mechanism by using poly(2-ethylhexyl acrylate) (P2EHA), which has a glass transition temperature of $\sim -60\,^\circ C$, as the membrane matrix.[31]

Determining more suitable membrane materials for PPLMs is both interesting and indispensible. To this end, poly(dodecyl methacrylate) (PC12MA), which has a glass transition temperature of $\sim -65\,^\circ C$, close to that of P2EHA,[35–37] was used as a candidate material for a PPLM. The transport of KCl through a PPLM made from PC12MA and dibenzo-18-crown-6 (DB18C6) and the chiral separation of a racemic mixture of phenylglycine (Phegly) through a PC12MA and O-allyl-N-(9-anthracenylmethyl)cinchonidinium bromide (AAMC) membrane were investigated.

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EXPERIMENTAL PROCEDURE

Materials

Dodecyl methacrylate (C12MA) was purified using vacuum distillation.[38] Benzyl 2-bromo-2-methylpropionate was prepared from 2-bromo-2-methylpropionyl bromide and benzyl alcohol.[39] Toluene, ethyl acetate and chloroform ($CHCl_3$) were purified using conventional methods.[40] CuBr, N,N,N',N',N''-pentamethyl diethylenetriamine, ethanol, hexane, DB18C6, KCl, AAMC, D-Phegly and L-Phegly were obtained from commercial sources, and were used as received. Tetrahydrofuran, HPLC grade, were purchased and were used without further purification. Water that was purified by an ultrapure water system (Simpli Lab, Millipores S. A., Molsheim, France) was used.

AAMC
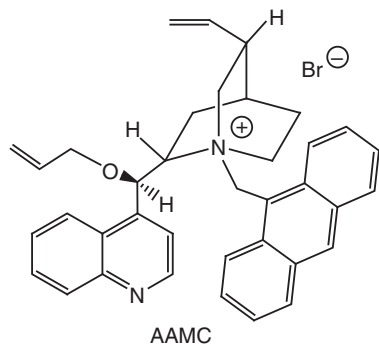
Preparation of PC12MA

The polymerization scheme is shown in Figure 1. The atom transfer radical polymerization of C12MA was conducted as follows: 10.00 g (3.93×10^{-2} mol) of C12MA, 11.0 cm³ of ethyl acetate and 255.6 mg (1.47×10^{-3} mol) of a ligand (N,N,N',N',N''-pentamethyl diethylenetriamine) were mixed together in a two-neck flask. The solution was purged under a nitrogen flow for at least 60 min; then, 211.4 mg (1.47×10^{-3} mol) of CuBr was added. The solution was stirred for 60 h and heated to a reaction temperature of 70 °C in an oil bath, after which 126.3 mg (4.91×10^{-4} mol) of the initiator benzyl 2-bromo-2-methylpropionate was added dropwise. The reaction was stopped by cooling the solution to ambient temperature, adding an excess of ethyl acetate and stirring it under air. The catalyst was removed *via* filtration over a neutral aluminum oxide. The solvent was evaporated, and the PC12MA was redissolved in 5 cm³ of $CHCl_3$ and precipitated in ethanol/hexane (2/1, v/v ratio), which was maintained at ~ -70 °C. The resulting precipitate was collected. The obtained polymer was then dried *in vacuo*, and 4.083 g (40.8%) of PC12MA was obtained.

Characterization of PC12MA

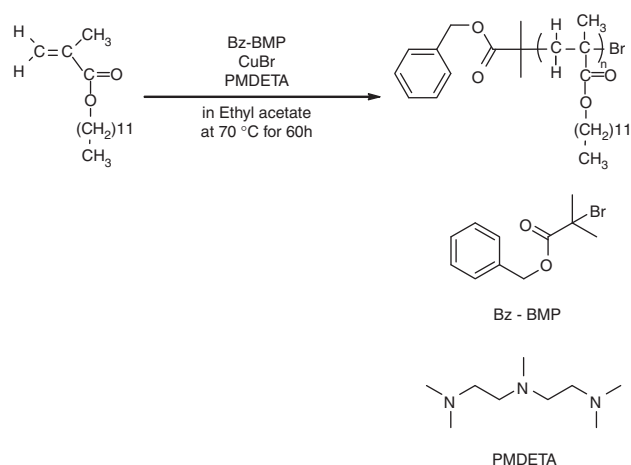Gel permeation chromatography was performed on a liquid chromatography system (JASCO Co., Hachioji, Japan) that was composed of a PU-2089 HPLC pump and an 860-CO column oven (operated at 35 °C) and equipped with JASCO 870-UV and Shodex RI-101 RI detectors (Showa Denko K.K., Tokyo, Japan). Polystyrene standards (Tosoh Co., Tokyo, Japan) were used for calibration, and tetrahydrofuran was used as an eluent at a flow rate of 1.0 cm³ min⁻¹.

Differential scanning calorimetry measurements were performed on a Shimadzu DSC-60 (Shimadzu Co., Kyoto, Japan). The heating rate was fixed at 10 °C min⁻¹, and the sample was purged with nitrogen at a flow rate of 50 cm³ min⁻¹.

Preparation of PPLMs

The PPLMs for KCl transport were prepared as follows: approximately 100.0 mg of PC12MA and the prescribed amount of DB18C6, which was ~ 2.5, 5.0 or 7.5 mg, were dissolved in 1.0 cm³ of $CHCl_3$. The prepared polymer solution was then poured into a flat laboratory dish (48 mm in diameter), followed by the immersion of a polytetrafluoroethylene (PTFE) membrane filter (Omnipore Membrane Filter, Millipore Corporation (Billerica, MA, USA); diameter of 47 mm; pore radius of 0.10 μm; porosity of 0.80; and thickness of 80 μm) into the cast solution. The flat laboratory dish was then evacuated in a desiccator to enable the cast solution to thoroughly penetrate into the pores of the PTFE membrane filter. The solvent was allowed to evaporate for 5 h at 25 °C and for an additional 24 h at 40 °C.

A control membrane was prepared as follows: 100.0 mg of PC12MA was dissolved in 1.0 cm³ of $CHCl_3$. The PPLM control membrane was constructed from the solution as described above.

A PPLM for chiral separation was prepared as described above. Instead of DB18C6, 2.5 mg of AAMC was used as the transporter for the chiral separation of a racemic mixture of Phegly.

KCl transport

The transport of KCl through the membrane was studied using the apparatus schematically shown in Figure 2. The PTFE filter membrane that was impregnated with PC12MA was tightly secured with parafilm between the two chambers of a permeation cell. The PTFE filter thickness, 80 μm, was used as the membrane thickness for this study. In the present study, the membrane area of the PTFE filter membrane was 3.0 cm², the effective membrane area was 2.4 cm², and the volume of each chamber was 40.0 cm³. A 1.0×10^{-4} mol cm⁻³ KCl aqueous solution was placed in the left-hand side chamber, and deionized water was placed in the right-hand side chamber (R-side). Transport experiments were conducted at 40 °C (313 K), 30 °C (303 K), and 20 °C (293 K). The aqueous solutions in both chambers were stirred by magnetic stirrers. The revolution rate of the magnetic stirrer was maintained as constant as possible, although the rate could not be determined. The KCl concentration in the permeate side (R-side) was determined by conductometric analysis using a Portable Kohlrausch Bridge TYPE BF-62A
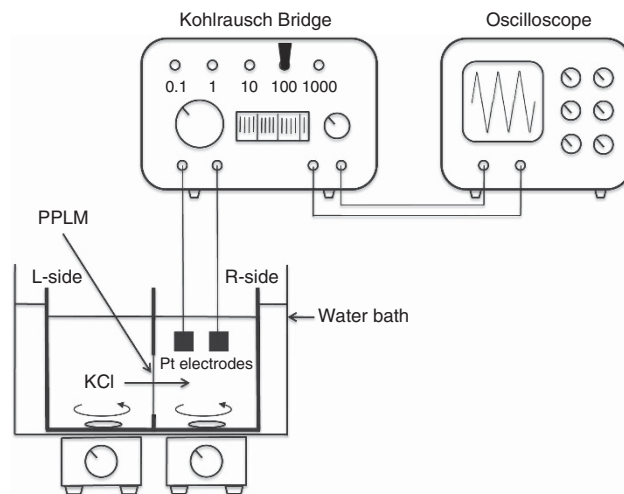

Figure 1 PC12MA polymerization scheme.

Figure 2 Schematic representation of the KCl transport setup.

(Shimadzu Rika Instruments Ltd., Kyoto, Japan) and a CO-1305 oscilloscope (KENWOOD Co., Yokohama, Japan), which is schematically shown in Figure 2.

Chiral separation of Phegly

An aqueous solution of racemic Phegly was placed in the left-hand side chamber and an aqueous solution was placed in the right-hand side chamber. The racemic Phegly concentration was fixed at $1.0 \times 10^{-6}\,\mathrm{mol\,cm^{-3}}$. The transport experiment was conducted as described above at a constant temperature of 40 °C. The pH condition of the source phase (left-hand side chamber) was maintained at 11 using Na_2HPO_4/NaOH, and that of the receiving phase was maintained at pH 3 using H_3PO_4/NaH_2PO_5.

The amounts of D- and L-Phegly that were transported through the membrane were determined by liquid chromatography (JASCO PU-2080, equipped with a ultraviolet detector (JASCO UV-2075)) using a CROWNPAK CR(+) column (Daicel Co., Osaka, Japan) (150 × 4.0 mm (i.d.)) and aqueous $HClO_4$ (pH 1.0) as an eluent.

The permselectivity $\alpha_{L/D}$ is defined as the flux ratio J_L/J_D divided by the concentration ratio [L-Phegly]/[D-Phegly]:

$$\alpha_{L/D} = (J_L/J_D)/([L - Phegly]/[D - Phegly]) \tag{1}$$

RESULTS AND DISCUSSION

Preparation of PC12MA

The number-average molecular weight of PC12MA, M_n, was 2.01×10^4, and its polydispersity index, M_w/M_n, was 1.16.

Figure 3 shows the obtained differential scanning calorimetry thermogram of PC12MA. The glass transition temperature (T_g) of the polymer was determined to be −66.3 °C, which coincides with the reported value.[35–37] The differential scanning calorimetry result revealed that the PC12MA prepared in the present study exhibited a rubbery state at the membrane transport operation temperature of 40 °C. It was expected that the membrane performance through the PC12MA PPLM would be comparable with that through the previous P2EHA membrane,[31] which had a glass transition temperature of ∼ −60 °C.

Transport of KCl through the membranes

DB18C6 was used as a model transporter and KCl was used as a target substrate to compare the membrane performance of PC12MA with previous results.[30,31] Figure 4 shows the time-transport curves of KCl through the three types of PPLM that consist of PC12MA and DB18C6 and through the corresponding control membrane. The straight line for each transport curve in Figure 4 was regarded as the steady state for each transport experiment. KCl was slightly
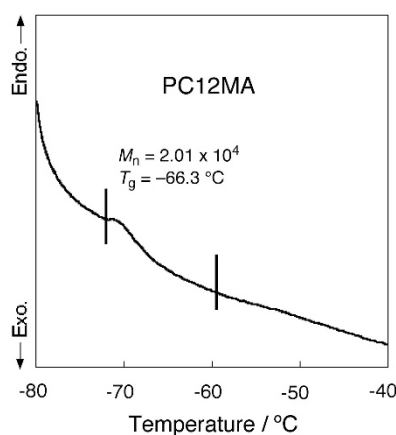
transported through the control membrane, that is, the simple diffusion of KCl, the diffusion of free ions and uncomplexed ion pairs through the membrane, was observed.

In the case of the transport of a uni-univalent salt, such as KCl, in which the salt is transported through a given liquid membrane simultaneously by simple diffusion and by facilitated transport, the flux of the uni-univalent salt can be represented by the following equation.[41,42]

$$J_{C,obsd} = (D_{CA}k/\delta)[K^+]^2 + (D_{CLA}kK[DB18C6]/\delta)[K^+]^2 \tag{2}$$

The fact that the transport of K^+ through a PPLM is represented by equation 2 was shown using the P2EHA/DB18C6 system,[31] implying that membrane transport through a PPLM is attained by a carrier-diffusion mechanism.[41,42]

Figure 5 shows the flux dependence on the transporter concentration. The total flux of K^+ through the PPLM (J_C) exhibited a linear relation to the transporter concentration [DB18C6]. The relation held for the flux of the control membrane, which had a transporter concentration of zero.

It is interesting to compare the results obtained in the present study with previous results, such as those for PPLMs made from P2EHMA[30] and P2EHA,[31] for a supported liquid membrane,[43] and for a polymer inclusion membrane.[14] The membrane performances of these membranes are given as normalized fluxes and are summarized
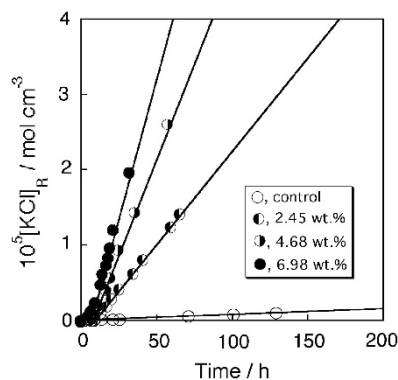

Figure 4 The time-transport curves of KCl through the PC12MA liquid membranes (operating temperature of 40 °C (313 K)).

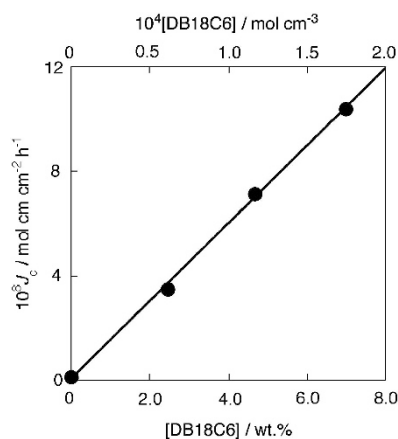**Figure 3** PC12MA differential scanning calorimetry thermogram.

Figure 5 Relation between the KCl flux and the DB18C6 concentration through the PC12MA liquid membranes at 40 °C (313 K).

Table 1 Comparison of the K^+ flux values for various membranes

| | J (normalized flux of K^+) | | |
| | $(mol \, cm \, cm^{-2} \, h^{-1})$ | | |
	$(mol \, cm^{-3})(mol \, cm^{-3})^2$	Ratio	Operating temp./$^{\circ}C$
PC12MA/DB18C6[a]	5.79×10^4	350	40
P2EHA/DB18C6[b]	5.88×10^3	35	40
P2EHA/DB18C6[c]	6.58×10^4	390	40
P2EHA/DB18C6[d]	1.33×10^5	800	40
P2EHMA/DB18C6[e]	6.20×10^3	37	40
CHCl3/DB18C6[f]	1.67×10^2	1	25
PIM/DC18C6[g]	2.37×10^2	1.4	25

[a]Present study; M_n of PC12MA $= 2.01 \times 10^4$.
[b]Cited from ref. 31; M_n of P2EHA $= 1.98 \times 10^4$.
[c]Cited from ref. 31; M_n of P2EHA $= 9.80 \times 10^3$.
[d]Cited from ref. 31; M_n of P2EHA $= 7.90 \times 10^3$.
[e]Cited from ref. 30; M_n of P2EHMA $= 2.50 \times 10^3$.
[f]Cited from ref. 43.
[g]Cited from ref. 14.

in Table 1. The normalized flux is the flux per unit membrane thickness per unit transporter concentration per square unit substrate concentration. The present PPLM gave a higher K^+ flux than the supported liquid membrane and the polymer inclusion membrane. Comparing the present membrane with the P2EHA PPLM, which had a molecular weight close to that of PC12MA, the normalized flux of the present membrane was ~ 10 times higher than that of the P2EHA one ($M_n = 1.98 \times 10^4$). The normalized flux of the PC12MA membrane was also ~ 10 times higher than that of the P2EHMA PPLM, which consisted of P2EHMA with a glass transition temperature of $-14.3 \, ^{\circ}C$. Contrary to this result, two other types of PPLM, which gave the molecular weight of P2EHA as 9.80×10^3 and 7.90×10^3, gave higher normalized flux values than the present membrane. The PC12MA PPLM, which has a molecular weight less than 1.0×10^4, should give higher normalized flux values than P2EHA membranes.

In our previous study, the apparent activation energies of K^+ transport through two types of PPLM were studied. In the present study, the apparent activation energy of K^+ transport through a PC12MA liquid membrane was determined, and its dependence on the glass transition temperature of the membrane matrix was also studied. Figure 6 shows the relation between the K^+ flux and the reciprocal of the absolute temperature. The slope of the straight line in the Arrhenius plot yields the apparent activation energy of the membrane transport. The apparent K^+ transport activation energy through the PC12MA PPLM was determined to be $32.7 \, kJ \, mol^{-1}$, which is slightly lower than that through P2EHA with a glass transition temperature of $-60.5 \, ^{\circ}C$. From this result, it is expected that the apparent activation energy of membrane transport would decrease with decreasing glass transition temperature for a given membrane matrix.

Application of PPLM for chiral separation
The results obtained in the present and previous studies[29–31] reveal that polymeric materials, which exhibit a rubbery state under the operating conditions, were applicable as membrane matrices for PPLMs. It is not only interesting but also indispensable to study other possible uses of these membrane matrices to expand the potential of PPLMs. To this end, the potential for enantioselective transport through a PC12MA membrane was investigated because
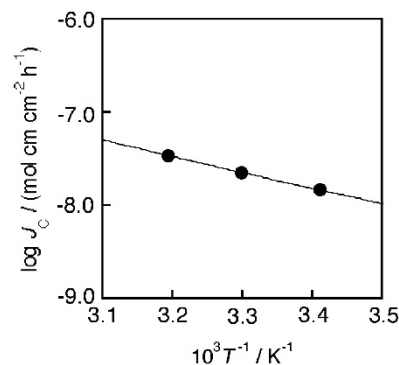
Figure 6 Temperature dependence of KCl transport through the PC12MA liquid membrane ([DB18C6] $= 6.13 \times 10^{-5} \, mol \, cm^{-3}$).
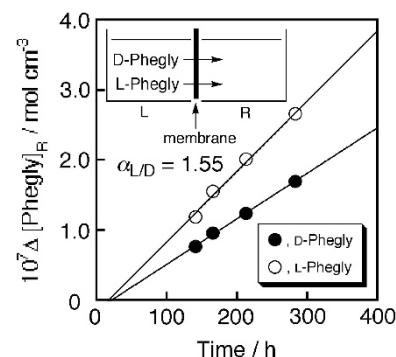
Figure 7 Chiral separation of the Phegly racemic mixture through the PC12MA liquid membrane at $40 \, ^{\circ}C$ (313 K).

chiral separation by a membrane is required in industries, such as pharmaceuticals, agrochemicals, food additives, perfumes, and so on.[44–47]

Cinchona alkaloids have been used as resolving agents for chiral binaphtols,[48] chiral acids,[49] amino acid derivatives[49,50] and oligopeptides.[51] Cinchona alkaloid was also used as a transporter for optical resolution.[52] On the basis of these studies, AAMC was chosen as a transporter for enantioselective transport, and the membrane performance was investigated using a racemic mixture of Phegly as a model racemate.

In the present study, AAMC with a cationic charge was used as a transporter to separate racemic mixtures of Phegly. On the basis of this setup, Phegly needed to be anionic to smoothly interact with the chiral transporter of AAMC at the interface, which was in contact with the source phase. Furthermore, the fast desorption of Phegly was required to release it from the membrane into the receiving phase at the interface between the membrane and the receiving phase. To this end, the pH value of the source phase was maintained at 11 and that of the receiving phase was maintained at pH 3.

Figure 7 shows the time-transport curves of racemic Phegly through the membrane. The L-isomer of Phegly was preferentially transported compared with the corresponding D-isomer. The permselectivity toward L-Phegly was determined to be 1.55, and the tentative transport mechanism is shown in Figure 8. Canepari et al.[52] reported that a liquid membrane consisting of AAMC and CHCl3 preferentially transported L-Phegly, and the permselectivity reached two. In that study, membrane transport was studied using a 'U' glass membrane; therefore, it is impossible to compare the membrane performances between the present study and that
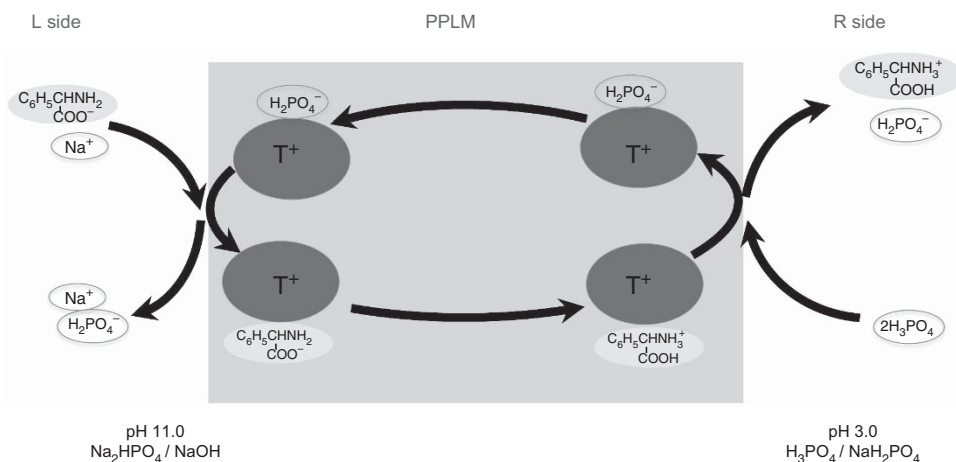
Figure 8 Tentative transport mechanism of the Phegly racemic mixture through the PC12MA liquid membrane. A full color version of this figure is available at *Polymer Journal* online.

reported by Canepari *et al.*[52] On the basis of the experimental conditions for chiral separation, the difference in the permselectivity in the present and the reported[52] studies may be mainly due to the differences in the affinities between L-Phegly and AAMC and between D-Phegly and AAMC in the membrane matrices with PC12MA and with CHCl₃.

The present study revealed that a PPLM was applicable not only to the transport of metal ions but also to the chiral separation of racemic mixtures, which was expected based on the transport mechanism of a PPLM. The incorporation of biological transporters into a PPLM will lead to novel separation membranes, and such a membrane system is expected to contribute to the understanding of unknown transporters that are found in biological membranes.

CONCLUSIONS

A PPLM was constructed from PC12MA, which exhibited a rubbery state under the membrane transport conditions and was used as the membrane matrix, and from DB18C6 or AAMC, which was used as a model transporter. KCl or a racemic mixture of Phegly was used as a model substrate to study membrane performance. The PPLM with DB18C6 transported KCl. The membrane transport ability depended on the DB18C6 concentration, implying that DB18C6 worked as a transporter within the PC12MA membrane matrix. L-Phegly was preferentially transported over D-Phegly through the membrane with AAMC from the racemic mixture of Phegly, and the permselectivity was determined to be 1.55. The present results suggest that PPLMs are applicable not only in metal ion transport but also in optical resolution.

D_{CA} = diffusion coefficient of the free solute ($cm^2 h^{-1}$)

D_{CLA} = diffusion coefficient of the complexed solute ($cm^2 h^{-1}$)

J_C = total flux of the diffusing solute, K^+, across the membrane per unit membrane thickness ($J_C = \delta \times J_{C,obsd}$) ($mol\, cm\, cm^{-2} h^{-1}$)

$J_{C,obsd}$ = observed total flux of the diffusing solute, K^+, across the membrane ($mol\, cm^{-2} h^{-1}$)

k = partition coefficient of the solute between water and the organic membrane ($mol^{-1} cm^3$)

K = equilibrium association constant ($mol^{-1} cm^3$)

δ = membrane thickness (cm)

[DB18C6] = total concentration of complexed and uncomplexed DB18C6 transporters in the membrane ($mol\, cm^{-3}$)

[K^+] = concentration of the diffusing solute, K^+, in the source phase ($mol\, cm^{-3}$)

1 Ho, W. S. W. & Sirkar, K. K. *Membrane Handbook* (Chapman & Hall, New York, USA, 1992).
2 Mulder, M. *Basic Principles of Membrane Technology.* 2nd edn. (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1996).
3 Baker, R. W. *Membrane Technology and Applications.* 2nd edn. (John Wiley & Sons, Ltd., West Sussex, England).
4 Danesi, P. R., Reichley-Yinger, L. & Rickert, P. G. Lifetime of supported liquid membranes: the influence of interfacial properties, chemical composition and water transport on the long-term stability of the membrane. *J. Membr. Sci.* **31,** 117–145 (1987).
5 Takeuchi, H., Takahashi, K. & Goto, W. Some observations on the stability of supported liquid membranes. *J. Membr. Sci.* **34,** 19–31 (1987).
6 Zha, F. F., Fane, A. G., Fell, C. J. D. & Schofield, R. W. Critical displacement pressure of a supported liquid membrane. *J. Membr. Sci.* **75,** 69–80 (1992).
7 Zha, F. F., Fane, A. G. & Fell, C. J. D. Instability mechanisms of supported liquid membranes in phenol transport process. *J. Membr. Sci.* **107,** 59–74 (1995).
8 Zha, F. F., Fane, A. G. & Fell, C. J. D. Effect of surface tension gradients on stability of supported liquid membranes. *J. Membr. Sci.* **107,** 75–86 (1995).
9 Yang, X. J. & Fane, A. G. Performance and stability of supported liquid membrabnes using LIX 984N for copper transport. *J. Membr. Sci.* **156,** 251–263 (1999).
10 Shinkai, S., Nakamura, S., Tachiki, S., Manabe, O. & Kajiyama, T. Thermocontrol of ion permeation through ternary composite membranes composed of polymer/liquid crystal/amphiphilic crown ethers. *J. Am. Chem. Soc.* **107,** 3363–3365 (1985).
11 Shinkai, S., Torigoe, K., Manabe, O. & Kajiyama, T. 'Complete' thermocontrol of ion permeation through ternary ocmposite membranes composed of polymer-liquid crystal-fluorocarbon-containing crown ethers. *J. Chem. Soc.: Chem. Commun.* 933–935 (1986).
12 Sugiura, M. Coupled-ion transport through a solvent polymeric membrane. *J. Colloid Interface Sci.* **81,** 385–389 (1981).
13 Sugiura, M., Kikkawa, M. & Urita, S. Effect of plasticizer on carrier-mediated transport of zinc ion gthrough cellulose triacetate membranes. *Sep. Sci. Technol.* **22,** 2263–2268 (1987).
14 Schow, A. J., Peterson, R. T. & Lamb, J. D. Polymer inclusion membranes containing macrocyclic carriers for use in cation separations. *J. Membr. Sci.* **111,** 291–295 (1996).
15 Riggs, J. A. & Smith, B. D. Facilitated transport of small carbohydrates through plasticized cellulose triacetate membranes. Evidence for fixed-site jumping transport mechanism. *J. Am. Chem. Soc.* **119,** 2765–2766 (1997).
16 Kusumocahyo, S. P., Kanamori, T., Sumaru, K., Aomatsu, S., Matsuyama, H., Teramoto, M. & Shinbo, T. Development of polymer inclusion membranes based on cellulose triacetate: carrier-mediated transport of cerium (III). *J. Membr. Sci.* **244,** 251–257 (2004).
17 Sgarlata, C., Arena, G., Longo, E., Zhang, D., Yang, Y. & Bartsch, R. A. Heavy metal separation with polymer inclusion membranes. *J Membr. Sci.* **323,** 444–451 (2008).
18 St John, A. M., Cattrall, R. W. & Kolev, S. D. Extraction of uranium(VI) from sulfate solutions using a polymer inclusion membrane containing di-(2-ethylhexyl)phosphoric acid. *J. Membr. Sci.* **364,** 354–361 (2010).
19 St John, A. M., Cattrall, R. W. & Kolev, S. D. Transport and separation of uranium(VI) by a polymer inclusion membrane based in di-(2-ethylhexyl)phosphoric acid. *J. Membr. Sci.* **409-410,** 242–250 (2012).
20 Neplenbroek, A. M., Bargenman, D. & Smoldres, C. A. *J. Membr. Sci.* **67,** 149–165 (1992).
21 Miyako, E., Maruyama, T., Kamiya, N. & Goto, M. *Membrane* **29,** 236–243 (2004).
22 Kemperman, A. J. B., Rolevink, H. H. M., Bargeman, D., van den Boomgaard, Th. & Strathmann, H. Stabilizationm of supported liquid membranes by interfacial polymerization top layers. *J. Membr. Sci.* **138,** 43–55 (1998).

23 Wang, Y., Thio, Y. S. & Doyle, F. M. Formation of semi-permeable polyimide skin layers on the surface of supported liquid membranes. *J. Membr. Sci.* **147,** 109–116 (1998).

24 Wijers, M. C., Jin, M. & Wessling, M. Strathmann, Supported liquid membranes modification with sulphonated poly(ether ether ketone) Permeability, selectivity, and stability. H. *J. Membr. Sci.* **147,** 117–130 (1998).

25 Fortunato, R., Afonso, C. A. M., Rels, M. A. M. & Crespo, J. G. Supported liquid membranes using ionic liquids: study of stability and transport mechanisms. *J. Membr. Sci.* **242,** 197–209 (2004).

26 Rios, A. P. de I, Hermandez-Fernandez, F. J., Thomas-Alonso, F., Palacios, J. M., Gomez, F., Rubio, M. & Villora, G. A SEM-EDX study of highly stable supported liquid membranes based on ionic liquids. *J. Membr. Sci.* **300,** 88–94 (2007).

27 Pirkle, W. H. & Doherty, E. M. Enantioselective transport through a silicone-supported liquid membrane. *J. Am. Chem. Soc.* **111,** 4113–4114 (1989).

28 Meier, W., Nardin, C. & Winterhalter, M. Reconstruction of channel proteins in (polymerizeds) ABA triblock copolymer membranes. *Angew. Chem. Int. Ed.* **39,** 4599–4602 (2000).

29 Sakiyama, T., Aoki, T. & Yoshikawa, M. ABA triblock copolymer POE-*block*-PDMS-*block*-POE as a component for liquid membranes. *Membrane* **29,** 377–383 (2004).

30 Naito, D., Yoshikawa, M., Maeda, S. & Okushita, H. Polymeric pseudo-liquid membranes from poly(2-ethylhexyl methacrylate). *Polym. J.* **41,** 1005–1010 (2009).

31 Murai, Y., Asaoka, S. & Yoshikawa, M. Polymeric pseudo-liquid membrane as a stable liquid membrane–evidence for carrier-diffusion mechanism. *J. Membr. Sci.* **380,** 216–222 (2011).

32 Ho, S. V., Sheridan, P. W. & Krupetsky, E. Supported polymeric liquid membranes for removing organics from aqueous solutions I. Transport characteristics of polyglocol liquid membranes. *J. Membr. Sci.* **112,** 13–27 (1996).

33 Harriott, P. & Ho, S. V. Mass transfer analysis of extraction with a supported polymeric liquid membrane. *J. Membr. Sci.* **135,** 55–63 (1997).

34 Ho, S. V. A supported polymeric liquid membrane process for removal of carboxylic acids from a waste stream. *Environ. Prog.* **18,** 273–279 (1999).

35 Rogers, S. S. & Mandelkern, L. Glass formation in polymers. I. The glass transitions of the poly(n-alkyl methacrylats). *J. Phys. Chem.* **61,** 985–990 (1957).

36 Lal, J. & Trick, G. S. Glass transformation temperatures of poly(vinyl alkyl ethers) and poly(vinyl alkyl sulfides). *J. Polym. Sci.* **A2,** 4559–4572 (1964).

37 Schneider, H. A. Polymer glass specificity of the glass temperature. *Polymer* **46,** 2230–2237 (2005).

38 Perrin, D. P. & Armarego, W. L. F. *Purification of Laboratory Chemicals.* 3rd edn. (Pergamon Press, Ocford, 1988).

39 Haddleton, D. M. & Waterson, C. Phenolic ester-based initiators for transition metal mediated living polymerization. *Macromolecules* **32,** 8732–8739 (1999).

40 Riddick, J. A., Bunger, W. B. & Sakano, T. K. *Organic Solvents.* 4th edn. (Wiley, New York, 1986).

41 Reusch, C. F. & Cussler, E. L. Selective membrane transport. *AIChE J* **19,** 736–741 (1973).

42 Lamb, J. D., Christensen, J. J., Izatt, S. R., Bedke, K., Astin, M. S. & Izatt, R. M. Effects of salt concentration and anion on the rate of carrier-facilitated transport of metal cations through bulk liquid membranes containing crown ethers. *J. Am. Chem. Soc.* **102,** 3399–3403 (1980).

43 Igawa, M., Tanaka, M., Izumi, S., Kaneko, Y. & Yamabe, T. Separation of potassium and sodium by liquid membrane. *Nippon Kagaku Kaishi* **1980,** 135–140 (1980).

44 Afonso, C. A. M. & Crespo, J. G. Recent advances in chiral resolution through membrane-based approaches. *Angew. Chem. Int. Ed.* **43,** 5293–5295 (2004).

45 Maier, N. M. & Linder, W. Chiral recognition applications of molecularly imprinted polymers: a critical review. *Anal. Bioanal. Chem.* **389,** 377–397 (2007).

46 Xie, R., Chu, L. -Y. & Deng, J. -G. Membranes and membrane processes for chiral resolution. *Chem. Soc. Rev.* **37,** 1243–1263 (2008).

47 Higuchi, A., Tamai, M., Ko, Y. -A., Tagawa, Y., Wu, Y. -H., Freeman, B. D., Bing, J. -T., Chang, Y. & Ling, Q. -D. Polymeric membranes for chiral separation of pharmaceuticals and chemicals. *Polym. Rev.* **50,** 113–142 (2010).

48 Rosini, C., Altemura, P., Pini, D., Bertucci, C., Zullino, G. & Salvadori, P. Cinchona alkaloids for preparing new, easily accessible chiral stationary phases II. Resolution of binaphthol derivatives on silica-supported quinine. *J. Chromatogr.* **348,** 79–87 (1985).

49 Mandl, A., Nicoletti, L., Lämmerhofer, M. & Landner, W. Quinine versus carbamoylated quinine-based chiral anion exchangers A comparison regarding enantioselectivity for N-protected amino acids and other chiral acids. *J. Chromatogr. A* **858,** 1–11 (1999).

50 Franco, P., Blanc, J., Oberleitner, W. R., Maier, N. M., Lindner, W. & Minguillon, C. Enantiomer separation by countercurrent chromatography using cinchona alkaloid derivatives as chiral selectors. *Anal. Chem.* **74,** 4175–4183 (2002).

51 Czerwenka, C., Lämmerhofer, M., Maier, N. M., Rissanen, K. & Lindnedr, W. Direct high-performance liquid chromatographic separation of peptide enantiomers: study on chiral recognition by systematic evaluation of the influence of structural features of the chiral selectors on enantioselectivity. *Anal. Chem.* **74,** 5658–5666 (2002).

52 Canepari, S., Girelli, A. M., Mattei, E. & Tosti, D. Enantioselective transport of D,L-phenylalanine and D,L-phenylglycine through a bulk liquid membrfane containing cinchona alkaloid derivatives as chiral selectors. *J. Braz. Chem. Soc.* **20,** 429–436 (2009).