

Polymeric Pseudo-Liquid Membranes from Poly(2-ethylhexyl methacrylate)

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Novel liquid membranes, which are named polymeric pseudo-liquid membranes, were constructed, using poly(2-ethylhexyl methacrylate), which showed rubbery state under operation conditions, as a membrane matrix. Dibenzo-18-crown-6 (DB18C6) was adopted as a model transporter and membrane transport performance through those polymeric pseudo-liquid membranes was investigated, adopting KCl as a model substrate. Poly(2-ethylhexyl methacrylate), P2EHMA, gave self-standing liquid membranes under the experimental conditions, of which operation temperature was above its glass transition temperature. The polymeric pseudo-liquid membranes showed transport ability of KCl. The flux value was linearly increased with the increase in DB18C6 content in the membrane and the membrane transport ability was greatly dependent on not only the molecular weight of membrane matrix, P2EHMA, but also the operation temperature. The present paper suggested that polymeric pseudo-liquid membranes are applicable to membrane separation as one of liquid membrane transport systems.

KEY WORDS: Crown Ether / Liquid Membrane / Poly(2-ethylhexyl methacrylate) / Polymeric Pseudo-Liquid Membrane / Rubbery Polymers / Transport /

Separation of a targeted substrate from a mixture containing compounds with similar molecular dimensions and showing similar chemical and/or physical properties is a difficult task in chemical industry. Such a targeted substrate, in general, has been separated by chromatography, especially liquid chromatography, which is usually operated as a batch process. Applying membrane separation technology to this field, the targeted molecule can be continuously separated from a mixture. In this case, membranes applied to separation should have molecular recognition sites or molecular recognition materials, which render them capable of separating substrates having similar molecular dimensions and properties. There are two ways to give membranes ability to separate quite similar substrates; one is a liquid membrane with a transporter for a target molecule, the other a fixed carrier membrane with a molecular recognition site or a molecular recognition material, which is covalently attached to the membrane material. Construction of liquid membrane is easier than that of a latter one, while there has been a drawback leading to the instability of liquid membranes. Generally liquid membrane has drawback in long-term stability, which is attributed to partial dissolution of the solvents, leaching of the carriers, and that of carrier-substrate complex.¹⁻⁶ It is an important and interesting subject to develop stable and defect-free liquid membranes so that neither membrane solvent nor transporter may be lost to the aqueous phases. To this end, there have been reported various types of durable liquid membranes, such as 1) polymer liquid crystal composite membranes,^{7,8} 2) polymer inclusion membranes,⁹⁻¹² 3) organogel membranes,^{13,14} 4) supported polymeric liquid membranes,¹⁵⁻¹⁸ 5) stabilization of top layer of supported liquid membranes by interfacial polymerization¹⁹⁻²¹

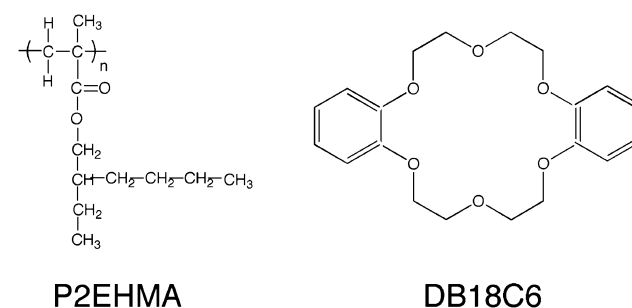


Figure 1. Chemical structures of P2EHMA and DB18C6.

or plasma polymerization,²² and 6) polymeric pseudo-liquid membranes.^{23,24} In the case that a candidate material with rubbery state under the operation condition gives durable self-standing membranes, such a rubbery material could be applicable to the membrane matrix of polymeric pseudo-liquid membrane. In the present paper, poly(2-ethylhexyl methacrylate) with glass transition temperature of around -10°C was adopted as a candidate membrane matrix for a novel polymeric pseudo-liquid membrane. The membrane performance of the polymeric pseudo-liquid membrane from poly(2-ethylhexyl methacrylate) was studied adopting dibenzo-18-crown-6 as a model transporter (Figure 1).

EXPERIMENTAL

Materials

2-Ethylhexyl methacrylate (2EHMA),²⁵ 2,2'-azobis(2-methylpropanitrile) (AIBN)²⁶ and toluene²⁷ were purified by

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Table I. Conditions and results for the syntheses of P2EHMA^a

	2EHMA		AIBN		Toluene	P2EHMA		10 ⁻³ M _n	M _w /M _n ^b
	g	mol	g	mol	cm ³	g	%		
P2EHMA-500	10.007	5.046 × 10 ⁻²	4.412	2.522 × 10 ⁻²	50.0	6.089	60.8	2.5	1.7
P2EHMA-005	8.001	4.032 × 10 ⁻²	0.033	2.017 × 10 ⁻⁴	40.0	7.411	92.6	120.0	5.7

^aPolymerization temp., 45 °C; polymerization time, 120 h. ^bDetermined by GPC.

conventional methods. Dibenzo-18-crown-6 (DB18C6), ethanol, hexane, chloroform and KCl were obtained from commercial sources and used as received. Tetrahydrofuran (THF) of HPLC grade was purchased and used without further purification. Water purified with an ultrapure water system (Simpli Lab, Millipore S. A., Molsheim, France) was used.

Preparation of Poly(2-ethylhexyl methacrylate), P2EHMA

The solution polymerizations of 2EHMA were carried out in glass ampoules at 45 °C for 120 h. The ampoules containing the prescribed amounts of 2EHMA and AIBN were degassed three times by the usual freeze-thaw cycles under high vacuum and then sealed. The reaction mixture was poured into ethanol/hexane (= 2/1; vol./vol. ratio), which was kept around -50 °C, and filtered. The resulting precipitate was collected. The polymers thus obtained were dried *in vacuo*.

Characterization of P2EHMA

¹H NMR spectra were recorded on a BRUKER AVANCE 500 FT NMR with tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) analysis was performed on a Shodex GPC SYSTEM-21, equipped with TSK-GEL G3000HXL and G5000HXL (Tosoh co.). Polystyrene standards were used for calibration and THF as eluent at a flow rate of 1.0 cm³ min⁻¹. Differential scanning calorimetry (DSC) measurements were performed with Shimadzu DSC-60. The heating rate was fixed to be 20 °C min⁻¹ and the sample was purged with nitrogen at a flow rate of 50 cm³ min⁻¹. Measurements of dynamic viscoelastic properties and stress relaxation were carried out with a rotational rheometer, ARES (TA Instruments, Inc.) equipped with 25 mm-diameter-parallel plates. The temperature for measurement ranged from 40 to 140 °C and the angular frequency from 10⁻² to 10¹ rad s⁻¹. The frequency dependence curves of storage modulus *G'* and loss modulus *G''* of each sample at various temperatures can be superposed into master curves by shifting the curves along the frequency axis by a shift factor a_T. The temperature dependence of a_T for two samples can be represented by the WLF type equations as follows:²⁸

P2EHMA-005:

$$\log a_T = -18.2(T - T_r)/(209 + T - T_r), \quad T_r = 80 \text{ °C} \quad (1)$$

P2EHMA-500:

$$\log a_T = -9.62(T - T_r)/(183 + T - T_r), \quad T_r = 80 \text{ °C} \quad (2)$$

Preparation of Polymeric Pseudo-Liquid Membranes

Control membranes were prepared as follows: 700.0 mg of P2EHMA was dissolved in 3.50 cm³ of CHCl₃; the polymer

solution thus prepared was poured into a TeflonPFA 75 mm diameter laboratory dish, and the solvent was allowed to evaporate at 25 °C for 5 h. The obtained membrane was dried at 50 °C for an additional 24 h.

Polymeric pseudo-liquid membranes were prepared as follows; 700.0 mg of P2EHMA and the prescribed amount of DB18C6, of which amount was 17.5 mg, 35.0 mg, or 70.0 mg, were dissolved in 3.50 cm³ of CHCl₃. Polymeric pseudo-liquid membranes were constructed from the polymer solution thus prepared as described above.

The thickness of the membrane was around 130 μm.

Transport Experiment

Transport of KCl through membrane was studied by the apparatus described in the previous paper.²⁴ The membrane was sandwiched between two filter papers and they were secured tightly with Parafilm between two chambers of a permeation cell. In the present study, the membrane area was 3.0 cm². The volume of each chamber was 40.0 cm³. 1.0 × 10⁻⁴ mol cm⁻³ of aqueous KCl solution was placed in the left-hand side chamber (L-side) and deionized water in the right-hand side chamber (R-side). Experiments were carried out at 25 °C, 32 °C and 40 °C, respectively. Aqueous solutions in both chambers were stirred by magnetic stirrers. Concentration of KCl in the permeate side (R-side) was determined by conductometric analysis.

RESULTS AND DISCUSSION

Preparation of Poly(2-ethylhexyl methacrylate), P2EHMA

Results of polymerization are summarized in Table I. 2EHMA was polymerized at the mole ratios of radical initiator AIBN to 2EHMA of around 0.50 and 0.0050, respectively. The former P2EHMA was named P2EHMA-500 and the latter P2EHMA-005, respectively. From the radical polymerization conditions, it was expected that the molecular weight of the former was lower than the latter. To confirm this, GPC analyses of two types of P2EHMA's were carried out. The molecular weight (number average molecular weight) increased from 2.5 × 10³ to 1.2 × 10⁵ with the decrease in the mole ratio of AIBN to 2EHMA from 0.50 to 0.0050. Following the ratio of kinetic chain length calculated by adopting the concentration ratio of the radical initiator AIBN,²⁹ the molecular weight of the latter would be ten times larger than the former. However, it was determined to be around 50 from GPC data.

Figure 2 shows DSC thermographs of those two types of P2EHMA's. The values of glass transition temperatures (*T_g*) for those polymers were determined to be -14.3 °C for

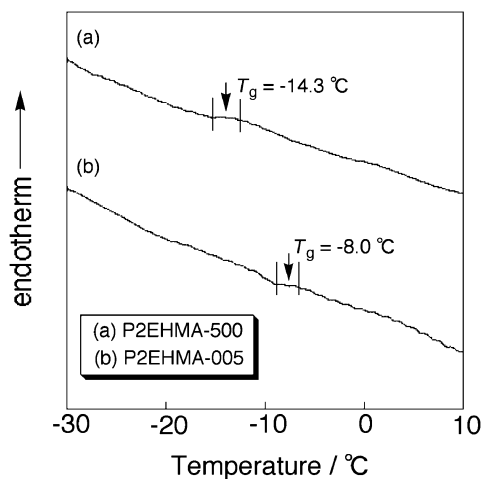


Figure 2. DSC thermographs of P2EHMA.

P2EHMA-500 and -8.0°C for P2EHMA-005, respectively. The results that T_g for P2EHMA-500 was lower than that for P2EHMA-005 are due to the fact that the molecular weight of the former was around one fiftieth lower than the latter. From DSC results, it was confirmed that those two types of P2EHMA's prepared in the present study showed rubbery state at the operation temperatures of membrane transport experiments in the present study.

The maximum relaxation times of P2EHMA-005 and P2EHMA-500 evaluated from stress relaxation curves are 1.9 s (at 140°C) and 6.5 s (at 80°C), respectively. Using the eq 1 and 2, the maximum relaxation times of P2EHMA-005 and P2EHMA-500 at 40°C are 4.5×10^8 s and 3.2×10^3 s, respectively.

From those results described above, a liquid membrane from P2EHMA-500 was expected to transport KCl faster than that from P2EHMA-005. Since the diffusion coefficients of both transporter and transporter-substrate complex can be thought to be inversely proportional to the viscosity of medium, which is semi-empirical relation and is based on the Stokes-Einstein equation.³⁰ This will be confirmed in the next section.

Transport of KCl through the Membranes

Membrane matrix forming ability of P2EHMA was investigated by adopting dibenzo-18-crown-6 (DB18C6) as a model transporter and KCl was adopted as a targeted substrate. Figure 3 shows time-transport curves of KCl through two types of polymeric pseudo-liquid membrane, consisting of P2EHMA-500 or P2EHMA-005. Those transport experiments were carried out at the constant temperature of 40°C . The straight line for each transport experiment in Figure 3 showed a transport curve of KCl, which was regarded as steady state for each experiment. As can be seen, KCl was slightly transported through both control membranes. Transport rate of KCl through membrane was increased with the increase in the amount of transporter in the membrane. Transport rate of KCl through P2EHMA-500 membrane seemed to be higher than that through P2EHMA-005 membrane. This might greatly

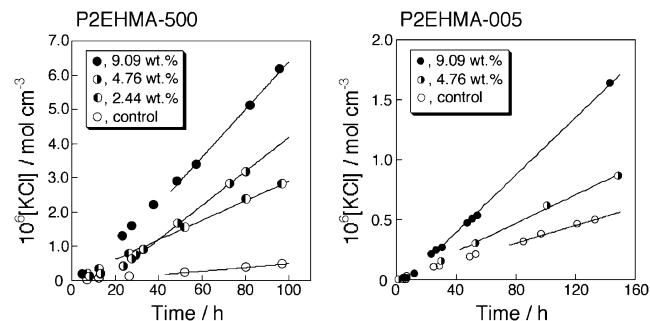


Figure 3. Time-transport curves of KCl through P2EHMA liquid membranes. (Operation temp., 40°C (313K).)

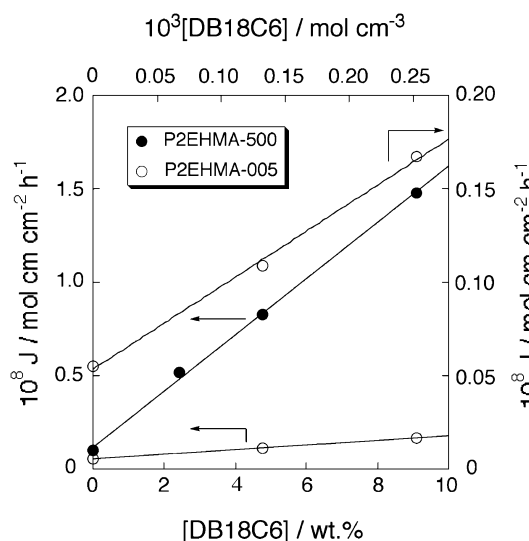


Figure 4. Relationship between KCl flux and DB18C6 concentration through P2EHMA liquid membranes.

attribute to the mobility of polymer chains, which was mainly governed by the difference in molecular weight. Figure 4 shows relationship between KCl flux through membrane and transporter concentration for two types of polymeric pseudo-liquid membrane. In the figure, the concentration of transporter DB18C6 was calculated, assuming the density of P2EHMA to be 1.0.³¹ As shown in Figure 3, both control membranes slightly transported KCl. KCl flux values for both membranes increased linearly with the increase in DB18C6 concentration. The dependence of KCl flux on transporter concentration can be represented by eq (3).^{32,33}

$$J_C = \frac{D_{CA}k}{\delta} C_{CS}^2 + \frac{D_{CLA}kK_{CL}}{\delta} \frac{C_{CS}^2}{1 + kK_{CS}^2} \quad (3)$$

From Figure 4, DB18C6 worked as a transporter in P2EHMA. In other words, P2EHMA played an important role as a liquid membrane matrix to isolate two aqueous phases, to dissolve transporter DB18C6 in it and to support DB18C6 to facilitate KCl transport through the membrane. In the present study, the transport rate of KCl through P2EHMA-500 liquid membrane was 12 times higher than that through P2EHMA-005 one. As

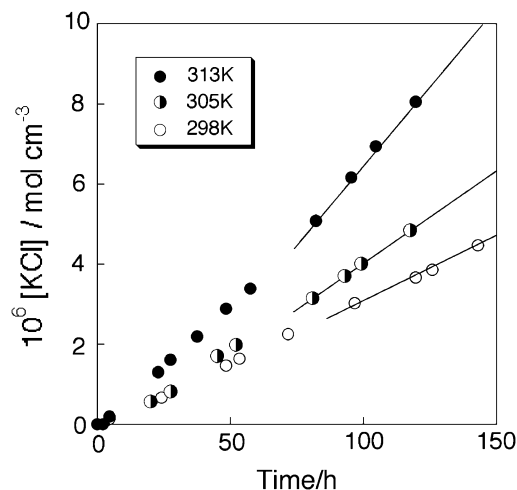


Figure 5. Dependence of KCl transport through P2EHMA-500 liquid membrane on operation temperature. (DB18C6 content in the membrane, 9.09 wt. %.)

expected in the previous section, P2EHMA-500 liquid membrane, of which molecular weight was lower than P2EHMA-005, gave higher flux than P2EHMA-005 membrane. As is well known, flux values are governed by two factors such as solubility and diffusivity following solution-diffusion theory.³⁴ In the present study, solubilities of KCl into two types of membranes were assumed to be same even though those two membranes had different molecular weights. Diffusivities of both the free solute (KCl) and the solute (KCl) complexed with transporter, which were greatly dependent on viscosity of medium, in P2EHMA-500 liquid membrane should be higher than those in P2EHMA-005 membrane. The difference in diffusivity of substrate KCl in the membrane was thought to be the dominant factor to determine transport flux of KCl. As a result, KCl was transported through P2EHMA-500 membrane faster than through P2EHMA-005 one.

If the membrane matrix showed glassy state under experimental conditions, KCl transport could be hardly observed. In addition, decrease in mobility of P2EHMA was expected to lead to decline of flux values of KCl transport. To this end, KCl transport through P2EHMA-500 with DB18C6 membrane was investigated at the operation temperature of 25 °C (298 K) and 32 °C (305 K) in addition to that of 40 °C (313 K). Time-transport curves at various operation temperatures are shown in Figure 5. As can be seen, the slopes of time-transport curves at a steady state decreased with the drop in the experimental temperature. As shown in Figure 6, Arrhenius plot of KCl flux versus reciprocal of absolute temperature yield apparent energies of activation of the membrane transport. The activation energy of KCl transport through P2EHMA-500 with DB18C6 membrane was determined to be 49.1 kJ mol⁻¹. At the moment, there have been few data of activation energy of KCl transport with polymeric pseudo-liquid membrane. In future, those values for various types of polymeric pseudo-liquid membranes will be considered in connection with T_g values of membrane matrices.

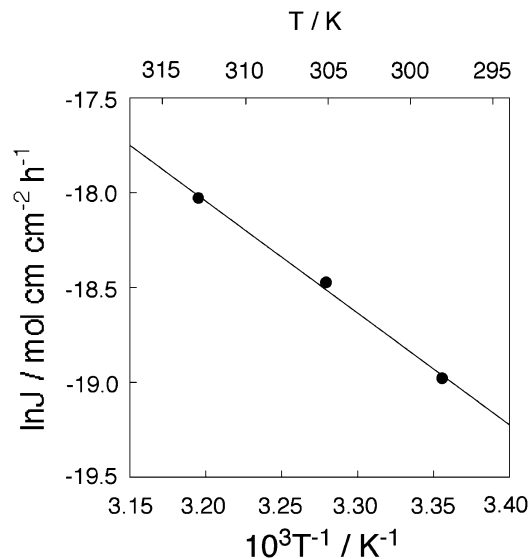


Figure 6. Temperature dependence of KCl transport through P2EHMA-500 liquid membrane. (DB18C6 content in the membrane, 9.09 wt. %.)

The transport result obtained in the present study was compared with those for other polymeric pseudo-liquid membranes previously studied in our laboratory, even though each operation temperature was different. The flux values at the transporter concentration of around 6.8×10^{-5} mol cm⁻³ for three types of membranes are summarized in Table II. In those studies, DB18C6 was adopted as a model transporter. As can be seen, the present membrane from P2EHMA gave relatively higher flux value. As for the future study, it can be expected that polymethacrylate or polyacrylate esters showing lower T_g values than that of P2EHMA have potentials to give liquid membranes showing higher transport ability.

CONCLUSIONS

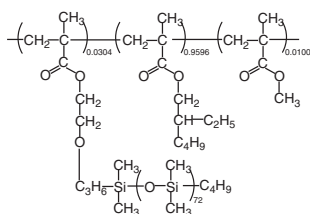
Novel liquid membrane systems were constructed, using poly(2-ethylhexyl methacrylate) (P2EHMA), which showed rubbery state under operation conditions, as a membrane matrix and dibenzo-18-crown-6 (DB18C6) as a model transporter. Those liquid membranes with rubbery polymers as membrane matrices were named polymeric pseudo-liquid membranes. The membrane performance was investigated, adopting KCl as a model substrate. P2EHMA gave self-standing liquid membranes under the experimental conditions, of which operation temperature was above its glass transition temperature. The present polymeric pseudo-liquid membranes transported KCl. The flux value was proportional to the DB18C6 concentration, implying that DB18C6 played as an important role of transporter in the membrane matrix of P2EHMA. The membrane transport ability was greatly governed by not only the molecular weight of membrane matrix, P2EHMA, but also the operation temperature. The present paper suggested that polymeric pseudo-liquid membranes are applicable to membrane separation as one of liquid membrane transport systems.

Table II. Summary of transport through the polymeric pseudo-liquid membranes

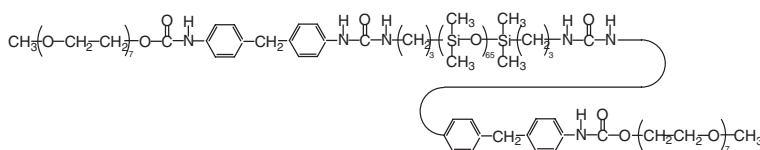
Polymer	[DB18C6]	Thickness	Area	J (ions)
	mol cm ⁻³	cm	cm ²	mol cm cm ⁻² h ⁻¹
P2EHMA-500 ^a	6.77 × 10 ⁻⁵	1.33 × 10 ⁻²	3.0	5.2 × 10 ⁻⁹ (KCl)
Comb copolymer ^b	6.80 × 10 ⁻⁵	3.3 × 10 ⁻³	3.0	4.9 × 10 ⁻¹¹ (KCl)
	6.80 × 10 ⁻⁵	2.6 × 10 ⁻³	3.0	1.6 × 10 ⁻¹¹ (NaCl)
ABA block copolymer ^c	6.80 × 10 ⁻⁵	5.0 × 10 ⁻³	4.5 × 10 ⁻⁵	3.1 × 10 ⁻¹⁰ (NaCl)

^aat 25 °C; present work. ^bat 30 °C; cited from ref 35. ^cat 60 °C; cited from ref 24.

Comb copolymer



ABA block copolymer



C_{CS} = concentration of the diffusing solutes in the source phase

C_L = total concentration of complexed and uncomplexed transporter in the membrane

D_{CA} = diffusion coefficient of the free solute

D_{CLA} = diffusion coefficient of the complexed solute

J_C = total flux of the diffusing solute across the membrane

k = partition coefficient of the solute between water and the organic membrane

K = equilibrium constant for the association

δ = membrane thickness

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 35. Unpublished data; part of results has been presented at ICOM2005 (Tu04E-1) and the Membrane Symposium 2004 (201) of the Membrane Society of Japan.