Studies on syntheses and permeabilities of special polymer membranes.
37. Permeabilities of poly(γ-methyl L-glutamate) membranes

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The permeation characteristics of poly(γ-methyl L-glutamate) (PMLG) membranes in the separation of polymers, poly(ethylene glycol) and poly(vinyl alcohol), from their aqueous solutions were influenced by the compaction of membrane swollen with water under pressure. The rate of pure water permeability up to an operating temperature of 70°C was governed by a change in the secondary-structure of PMLG. In addition, the permeabilities of alcohols through PMLG membrane were discussed.

Keywords Synthesis; permeability; polymer membranes; poly(α-methyl L-glutamate); secondary-structure

INTRODUCTION

Poly(γ-methyl L-glutamate) is a synthetic polypeptide. Its secondary-structures consist of an α-helix[1], β-structure[2], and random coil, which interconvert mutually[3] and have a variety which is not observed in general synthetic polymers. It is interesting to reveal the relationships between these changes of structure and the permeability through membranes. The higher-order structure and physical properties of synthetic polypeptide membranes have been studied by many workers[4-6]. There have been interesting presentations[7,8] on the sorption and the permeability of gases such as water vapour, carbon dioxide, alcohols, and xenon, etc. through poly(n-alkyl L-glutamate) membranes, but there are not many reports on liquid permeability of these membranes. We have reported previously the permeation characteristics of poly(γ-methyl L-glutamate) membranes, which were prepared by using the mixed solvent dichloroacetic acid and formamide as the casting solvent, in the separation of aqueous polymer solutions[9].

Here, the poly(γ-methyl L-glutamate) membranes are prepared from mixtures of poly(γ-methyl L-glutamate), *m*-cresol, and ethylene dichloride. The permeation characteristics of pure water and aqueous polymer solutions and the permeability of alcohols through these membranes are investigated under an applied hydrostatic pressure and discussed in connection with the physical deformation of membranes under pressure, the molecular conformations of the poly(γ-methyl L-glutamate) membranes, and the nature of the permeating molecules.

EXPERIMENTAL

Poly(γ-methyl L-glutamate) (PMLG) produced by Kyowa Hakko Co. Ltd., having an average degree of polymerization ($\overline{DP}$) of 1200, was employed as the membrane substance. Pure commercial *m*-cresol and ethylene dichloride (EDC) were used as solvents for the casting solutions. Methyl alcohol used as gelation medium or extraction solvent was a commercial reagent. Poly(vinyl alcohol) (supplied by Kurary Co. Ltd.) and poly(ethylene glycol) (supplied by Sanyo Kasei Co. Ltd.) used as solutes of feed solutions were PVA 205 and PEG 20000 whose $\overline{DP}$ were 550 ± 50 and 350 ± 50, respectively. All alcohols used as feed solutions were pure commercial sources.

Preparation of membranes

The casting solutions were prepared from systems of PMLG/*m*-cresol/EDC. The membranes were made by pouring the casting solutions onto a rimmed glass plate, allowing evaporation of the solvent at 25°C for 48 h, and immersing the glass plate together with the membranes into methyl alcohol (25°C). After 24 h in methyl alcohol, the membranes were removed from the glass plate, treated with methyl alcohol in a Soxhlet extractor for 24 h to remove the casting solvents completely, then heated at 40°C for 30 min, and then subjected to a pressure of 5 kg cm^{-2} for 30 min.

Apparatus and measurements

The apparatus and the experimental procedure have been reported previously[10-12]. The effective membrane area set in the cell was 12.0 cm^2. Unless otherwise stated the operating conditions in the permeation were 40°C, 2 kg cm^{-2}. All experiments lasted 2 h. The membrane thickness swollen with pure water was determined by means of the dial thickness gauge (Teclock Co.). All the membranes prepared were asymmetric. Therefore, the permeation rate could not be represented by considering the membrane thickness.

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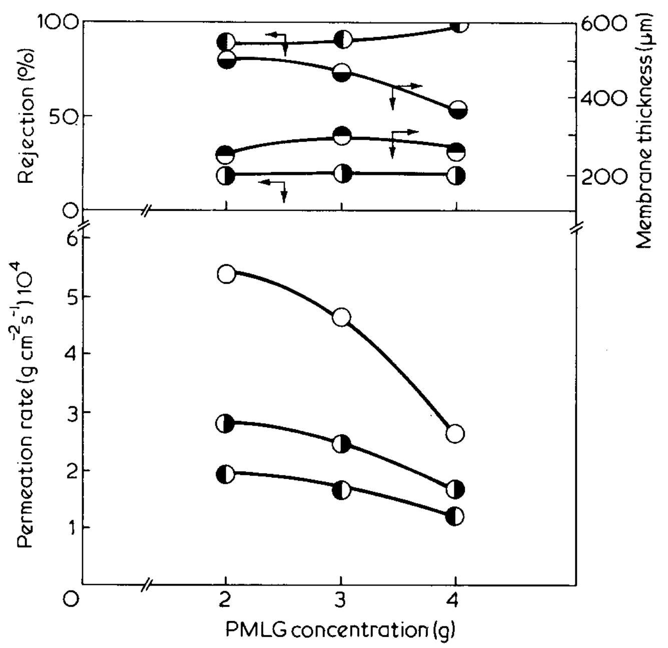

Figure 1 Effect of polymer concentration on permeation characteristics. Composition of casting solution: PMLG/*m*-cresol/EDC = *X*/50/50 (g); feed: (○) pure water, (◑) PEG 20000, (◐) PVA 205, 1% aqueous solutions; operating conditions: 40°C, 2 kg cm^{-2}; membrane thickness: (◒) before pressure treatment, (◓) after pressure treatment

RESULTS AND DISCUSSION

The effect of PMLG concentration in the casting solution on the permeation characteristics is shown in *Figure 1*, where the ratio *m*-cresol/EDC is kept constant at 50/50 (g) and the PMLG concentration is changed. The permeation rates for pure water, aqueous solutions of PEG 20000 and PVA 205 decrease with increase in PMLG concentration. Kleman *et al.*[13] and these authors[9,14] reported that the magnitude of the average pore radius decreases with an increase in concentration of cellulose acetate and PMLG. The rejections for PEG 20000 and PVA 205 increase slightly with the PMLG concentration. The results in *Figure 1* suggest that the membranes with higher PMLG concentration are denser than the membranes prepared from lower PMLG concentration. The thickness of membrane swollen with pure water decreases as the PMLG concentration increases. This result is dependent on the formation of a membrane having a very dense structure because polymer aggregation in the casting solution becomes stronger and swelling of the membrane in the gelation medium becomes smaller with increase in PMLG concentration. The fact that the difference between the membrane thicknesses before and after the pressure treatment decreases with the PMLG concentration suggests that the membrane prepared from higher PMLG concentration is difficult to compact under pressure.

Effect of composition of casting solution

The composition of casting solution affects the structure of the resulting membranes such as thickness, pore number, pore size, and crystallinity of skin layer of asymmetric membranes. The effect of composition of the casting solution on the permeation characteristics is shown in *Figure 2*, where the PMLG concentration is kept constant at 3 wt% and the ratio *m*-cresol/EDC is changed. As can be seen from *Figure 2*, the membrane thickness increases significantly with an increase in *m*-cresol content in the casting solution. The permeation rates for pure water, aqueous solutions of PEG 20000 and PVA 205 have a maximum value at *m*-cresol/EDC ratio of 60/37 (wt%) and the rejection for PVA 205 has a minimum at this ratio of the casting solvent.

As can be seen from the membrane thickness, the membranes obtained in this work are considerably swollen with water. This phenomenon is due to the fact that the resulting membranes are remarkably swollen with methyl alcohol because the casting solvents remain in the casting mixture in relatively large quantities and the cohesive forces of the PMLG molecules for methyl alcohol (gelation medium) are small. Therefore, there is a good correlation between the *m*-cresol content and the membrane thickness. The increase of permeation rates for pure water, aqueous solutions of PEG 20000 and PVA 205 with an increase in *m*-cresol content are attributed to a decrease in permeation resistance based on the increased degree of swelling of the membrane and caused by the decrease in thickness of the skin layer in the asymmetric membrane. This discussion is supported by the fact that the rejections for PEG 20000 and PVA 205 decrease slightly. In the ratio *m*-cresol/EDC of 70/26 (wt%), the decrease in the permeation rates for pure water and aqueous solutions and the increase of rejection for PVA 205 depend on the compaction of the membrane under pressure. This is understood by the fact that the difference in membrane thickness before and after the pressure treatment is significantly large.

Effect of operating temperature

Figure 3 shows the effect of operating temperature on the rate of pure water permeability. The numbers I, I′, II,

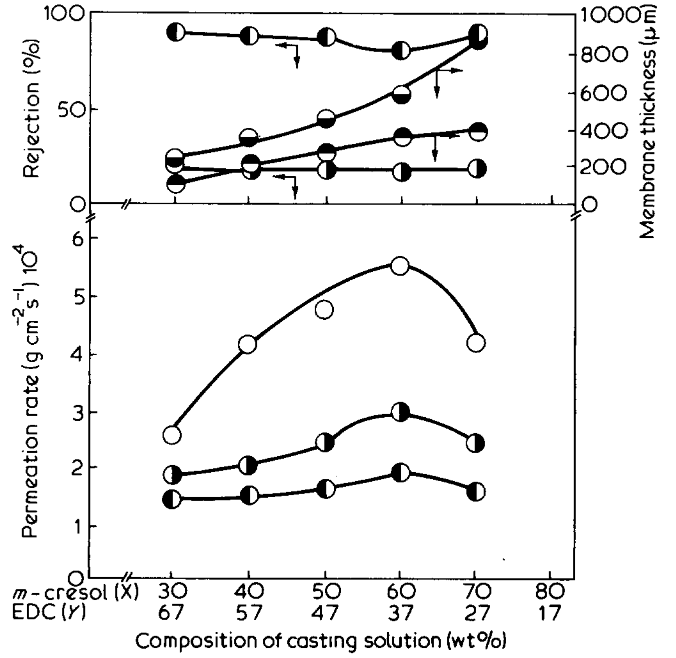

Figure 2 Effect of composition of casting solution on permeation characteristics. Composition of casting solution: PMLG/*m*-cresol/EDC = 3/*X*/*Y* (wt%); feed: (○) pure water, (◑) PEG 20000, (◐) PVA 205, 1% aqueous solutions; operating conditions: 40°C, 2 kg cm^{-2}; membrane thickness: (◒) before pressure treatment, (◓) after pressure treatment

and II′ represent the sequence of the operations, and the arrows indicate the direction of temperature change in each operation. The open circle and the full circle are the rate of pure water permeability for the membrane which is not heated and for the membrane that is heated at 90°C for 30 min, respectively. The increase in permeation rates for pure water up to 70°C are mainly caused by a decrease in viscosity of pure water and an activation of thermal motion of PMLG molecules. Alternatively, the decrease in rates of pure water permeability over 70°C in the operations I and I′ are primarily dependent on the increase in the membrane shrinkage and the crystallinity of the membrane. In operations II and II′ there is a decrease in permeation rates for pure water over 70°C although the degrees of decrease in the permeation rate are smaller than those in the operations I and I′. From these results it is found that the decrease in permeation rate in this range of operating temperature is reversible. Therefore, this decrease is not due to the shrinkage of membrane only. It is presumed that the higher-order structure of the PMLG membrane, in particular the second-order structure of PMLG molecules, affect the permeation rate of pure water.

Figure 4 shows the infra-red absorption spectra of the PMLG membranes measured by changing the temperature. The absorption band at 615 cm^{-1} is assigned to the amino absorption of the α-helix[15]. This absorption band is shifted to a lower wavenumber with an increase in measurement temperature. The characteristic absorption bands at 563 cm^{-1} and 720 cm^{-1} are due to the α-helix structure. These bands decrease with temperature. These changes of absorption bands support the change of structure of the PMLG membrane and are reversible with temperature. This reversibility agrees well with the fact (*Figure 3*) that the rate of pure water permeability is reversible with operating temperature. Consequently, the decrease in permeation rate for pure water in the range of 80°–90°C may be caused by part of the α-helix of PMLG being converted into the β-structure.

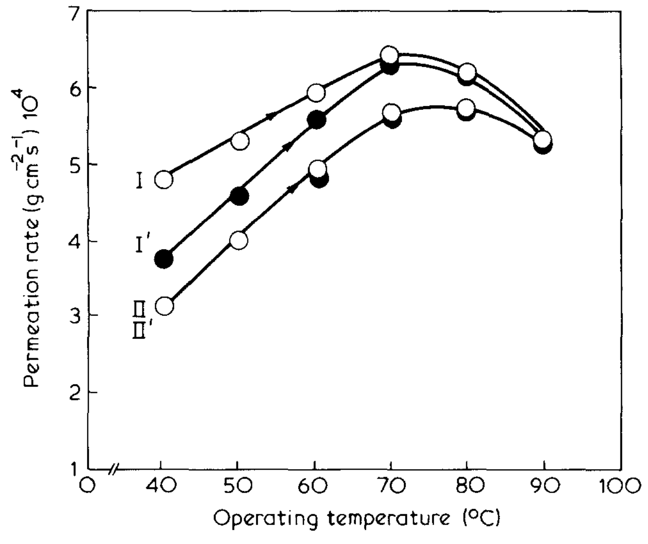

Figure 3 Effect of operating temperature on rate of water permeability. Composition of casting solution: PMLG/*m*-cresol/EDC = 3/50/47 (wt%); feed: pure water; operating pressure: 2 kg cm^{-2}; (○) unheated membrane; (●) membrane treated with heat (90°C, 30 min)

Effect of permeant

Table 1 summarizes the effect of molecular length, molecular volume, solubility parameter, and viscosity of alcohols on the permeation rates. The permeation rates of linear alcohols are found to decrease with increase in the number of carbon atoms in the linear alcohol molecule. The permeabilities of linear alcohols and hydrocarbons

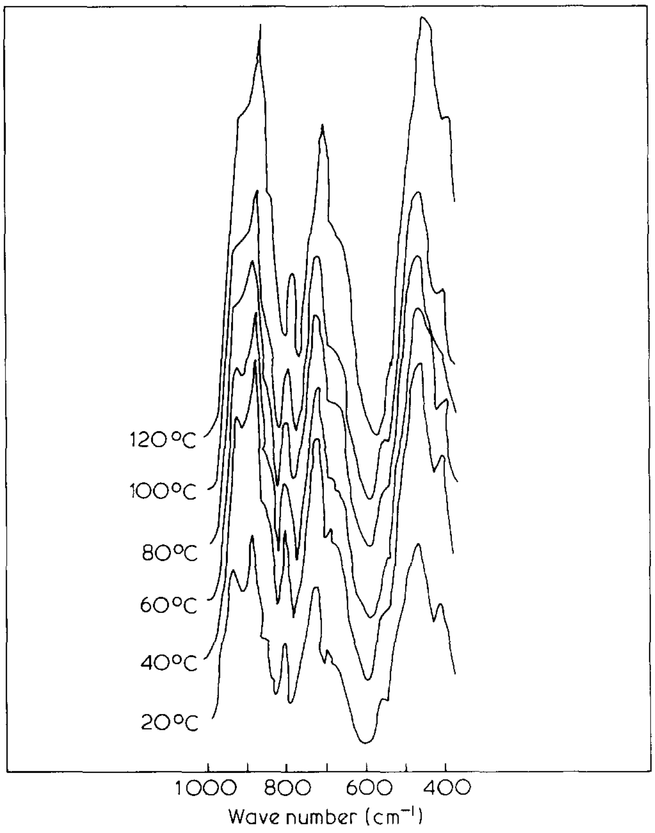

Figure 4 Infra-red spectra of PMLG membranes with change in measurement temperature

Table 1 Effect of molecular volume, molecular length, viscosity, and solubility parameter of alcohol on permeation rate

Permeant	Molecular volume $\bar{V}$ (Å^3)	Molecular length $\bar{L}$ (Å)	Cross section $\bar{V}/\bar{L}$	Viscosity η at 40°C (cP)	Solubility parameter (cal $cm^{-3})^{1/2}$	Permeation rate at 40°C (g cm^{-2} s^{-1})
CH_3OH	67.2	2.9	23.2	0.468	14.5	4.73×10^{-4}
C_2H_5OH	96.9	4.2	23.1	0.825	12.7	3.70×10^{-4}
n-C_3H_7OH	124	5.4	23.0	1.38	11.9	2.40×10^{-4}
n-C_4H_9OH	152	6.6	23.0	1.78	11.4	1.87×10^{-4}
n-$C_5H_{11}OH$	180	7.8	23.0	2.12	10.9	1.36×10^{-4}
iso-C_3H_7OH	127	4.3	29.5	1.33	11.5	2.25×10^{-4}

Composition of casting solution: PMLG/*m*-cresol/EDC=3/50/47 (wt%); operating conditions: 40°C, 2 kg cm^{-2}

through polyethylene[16], acrylonitrile–butadiene–styrene terpolymer[17], and nylon-12[18] membranes decrease as the number of carbon atoms in the alcohol and hydrocarbon molecule increases. From these results, it can be seeen that the permeation rate of a homologous series depends on the permeation resistance based on the molecular length and viscosity of the permeating species. The permeation rate decreases with a decrease in the solubility parameter of the permeating molecule, which plays an important role in liquid permeation. In general, a solvent with a solubility parameter δ very close to that of the polymer membrane substrate is absorbed to a larger extent than a solvent with a δ value which is far from that of the polymer membrane substrate. From these results, it is presumed that the solubility parameter of PMLG is close to that of a higher alcohol. The solubility parameter of dichloroacetic acid, which is the best solvent for the PMLG molecule, is 11.0[19]. This value supports the above assumption. The permeation rate of iso-propyl alcohol is lower than that of n-propyl alcohol. Huang *et al.*[20] reported that the permeation rates of isomer alcohols through cellulose membranes and poly(vinyl alcohol) membrane was dependent on the cross-section of the alcohol molecule. Fang *et al.*[21] reported that the order of separation from aqueous alcohol solution was n-, iso-, sec-alcohol using crosslinked poly(ethylene imine) membranes and was related to the cross-section of the alcohol molecule. As can be seen from *Table 1*, the permeation rate of the isomer alcohol depends not only on the cross-section[16,20], $\bar{V}/\bar{L}$, where $\bar{V}$ is the molecular volume and $\bar{L}$ is the maximum molecular length, but also on the viscosity and the solubility parameter of the isomer alcohol.

REFERENCES

1 Pauling, L. and Corey, R. B. *Proc. Natl. Acad. Sci. U.S. A.* 1951, **37**, 235; *Proc. Intern. Wool. Textile Res. Conf.* 1955, **B**, 249

2 March, R. E. and Pauling, L. *Biochem. Biophys. Acta.* 1955, **16**, 1

3 Doty, P., Bradbury, J. H. and Holtzer, A. H. *J. Am. Chem. Soc.* 1956, **78**, 947

4 Nakajima, A., Fujiwara, T., Hayashi, T. and Kaji, K. *Biopolymers* 1973, **12**, 2681

5 Mohadger, Y. and Wilkes, G. L. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 963

6 Hayashi, T. *Kobunshi Kagaku* 1978, **32**, 416

7 Takizawa, A. *et al. Kobunshi Kagaku* 1971, **28**, 751; *Polymer* 1974, **15**, 157; *J. Makromol. Sci. Phys.* 1975, **B11**, 121; *J. Appl. Polym. Sci.* 1974, **18**, 1443; 1978, **22**, 279

8 Minoura, N. and Nakagawa, T. *J. Appl. Polym. Sci.* 1979, **23**, 2729

9 Uragami, T., Kido, S. and Sugihara, M. *Tech. Rept. Kansai Univ.* 1979, **20**, 97

10 Uragami, T., Fujino, K. and Sugihara, M. *Angew. Makromol. Chem.* 1976, **55**, 29

11 Uragami, T., Tamura, M. and Sugihara, M. *Angew. Makromol. Chem.* 1976, **55**, 59

12 Uragami, T. and Sugihara, M. *Angew. Makromol. Chem.* 1977, **57**, 123

13 Kleman, K. and Friedman, L. *J. Am. Chem. Soc.* 1932, **54**, 2637

14 Uragami, T., Fujino, K. and Sugihara, M. *Angew. Makromol. Chem.* 1978, **68**, 39

15 Masuda, Y. *Kobunshi Kagaku* 1963, **20**, 161

16 Huang, R. Y. M. and Lin, V. J. C. *J. Appl. Polym. Sci.* 1968, **12**, 2615

17 Uragami, T., Yono, T. and Sugihara, M. *Angew. Makromol. Chem.* 1979, **82**, 89

18 Uragami, T., Maekawa, K. and Sugihara, M. *Angew. Makromol. Chem.* 1980, **87**, 175

19 'Polymer Handbook' (Ed. J. Brandrup), John Wiley and Sons, New York, 1966, p. IV–347

20 Huang, R. Y. M. and Jarvis, N. R. *J. Appl. Polym. Sci.* 1970, **14**, 234

21 Fang, H. H. P. and Chian, E. S. K. *J. Appl. Polym. Sci.* 1974, **18**, 2892