

Pervaporation of Ethanol–Water Mixtures through Styrene-Substituted *N*-Phenylmaleimide Copolymer Membranes

J. LOKAJ* and J. BÍLÁ

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

SYNOPSIS

A number of copolymers of styrene with substituted *N*-phenylmaleimides were synthesized and their solutions in chloroform were used in the casting of homogeneous membranes. The latter were applied in the separation of variously concentrated ethanol–water mixtures by pervaporation at 35°C. The membranes were characterized by the separation factor related to preferentially transported water and by the flux of the permeate. In contrast to membranes made from copolymers of styrene with *N*-phenylmaleimide, the separation factor of membranes containing substituted *N*-phenylmaleimides increased with increasing amount of ethanol in the feed solution. The effect of incorporated imide units on the properties of the membranes under investigation is discussed. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation of liquid mixtures consisting in the permeation of liquids through membranes followed by the removal of the permeate in the form of a vapor phase ranks among membrane processes that are studied with great attention.¹ It may be used in the dehydration of solvents, in the removal of liquid organic admixtures from water, or in the separation of mixtures of organic solvents. Great attention is devoted to the concentration of aqueous ethanolic solutions and to the purification of ethanol by the pervaporation techniques.² The chemical structure and physical properties of the membranes used play an important role in this process.³

Yoshikawa et al.⁴ report the separation of ethanol–water mixtures by pervaporation through membranes made from poly(styrene-co-*N*-phenylmaleimide). Membranes were selectively permeable to water. In the authors' view, the preferential water transport is connected with its interaction with carbonyl groups in the maleimide units, which as carriers facilitate the permeation of water compared with that of ethanol. We were interested in how pervaporation would proceed through mem-

branes based on copolymers of styrene with derivatives of *N*-phenylmaleimide. We intended to estimate the effect of the structure of incorporated maleimide units on the pervaporation properties of the polymeric membranes. For this purpose, we synthesized several copolymers of styrene with substituted *N*-phenylmaleimides and for membranes made from these copolymers determined pervaporation characteristics in the separation of water and ethanol.

EXPERIMENTAL

Materials

N-(3-Dimethylaminophenyl)maleimide (I) (m.p. 98°C), *N*-(2-methyl-5-dimethylaminophenyl)maleimide (II) (m.p. 86°C), *N*-(2,4,6-tribromophenyl)maleimide (III) (m.p. 142°C), *N*-(2,3,4,5,6-pentabromophenyl)maleimide (IV) (m.p. 215°C), *N*-(2,4,6-trichlorophenyl)maleimide (V) (m.p. 131°C), and *N*-(2,3,4,5,6-pentachlorophenyl)maleimide (VI) (m.p. 150°C) were prepared by the cyclodehydration of the corresponding maleamic acids.⁵ Styrene (S) (b.p. 36°C/1.56 kPa) and 2,2'-azobis(isobutyronitrile) (AIBN) (m.p. 105°C) were purified by a procedure reported earlier.⁶ Water–ethanol solutions were prepared from ethanol of UV spectroscopy purity. The solvents used were chromatographically pure.

* To whom correspondence should be addressed.

Synthesis of Styrene-Substituted *N*-Phenylmaleimide Copolymers

Reaction mixtures containing styrene (61 g), a *N*-phenylmaleimide (1 g), and AIBN (0.15 g) were heated at 50°C in an inert atmosphere in sealed glass ampoules. After 6 h copolymers were precipitated from the mixtures using a sixfold amount of ethanol. The copolymers were dried to constant mass at room temperature and 13.3 Pa and reprecipitated from benzene solutions with ethanol. Their composition was calculated from the content of C, H, and N. The conversions of the monomers (10–14%) were calculated from the composition and mass of the copolymers.

Preparation of the Membranes

The membranes were obtained by casting 10 wt % chloroform solutions of copolymers on glass plates up to 0.35 mm layer thickness. After evaporation of the solvent at room temperature the plates were immersed in water and films 30 μm thick were released.

Measurement

Pervaporation experiments were carried out using an apparatus, the main part of which was a cell with an inserted membrane, over which an ethanol–water mixture (200 mL) was circulating at 35°C. The composition of the mixture was determined pycnometrically. The active membrane area was 49 cm². On the side of the permeate a pressure of about 400 Pa was maintained by means of an oil pump. The permeate was collected in an ampoule cooled with liquid nitrogen and analyzed by GLC (Porapak Q, 1-propanol as the internal standard).

RESULTS AND DISCUSSION

Styrene-Substituted *N*-Phenylmaleimide Copolymers

Maleimides I through VI readily undergo radical copolymerization with styrene. In agreement with the reactivity ratios^{7,8} of pairs styrene–*N*-arylmaleimide, which are close to zero and high positive Alfrey-Price values e of these imides, the copolymerization was accompanied by a pronounced enrichment of the copolymers in imide compared with its content in the starting reaction mixture. The fraction of incorporated substituted *N*-phenylmaleimide compared with its fraction in the polymerization mixture increased from 9 to 13 times. The limiting viscosity

numbers of copolymers containing imides with the dimethylamino group I, II were higher than those of copolymers with halogenated *N*-phenylmaleimides III–VI (Table I). This phenomenon is obviously related with the polymer chain transfer to monomeric imide, operative in its homopolymerization and copolymerization.^{8,9} The $[\eta]$ values given in Table I indicate an easier polymer chain transfer to halogenated imides than to *N*-(dimethylamino-phenyl) maleimides and an easier transfer reaction in the case of a higher number of halogen atoms in imides IV and VI. Similarly,^{9,10} due to the transfer to monomer the homopolymerization of *N*-(halogenophenyl) maleimides yields only tetramers, while the average degree of polymerization of poly[*N*-(dimethylaminophenyl) maleimides] is 11–14.

Styrene-Substituted *N*-Phenylmaleimide Copolymer Membranes

Compact transparent membranes were prepared by casting from CHCl₃ or benzene solutions of copolymers. At an imide content in the copolymers higher than 30 wt % the membranes were brittle and fragile.

Membranes with incorporated imides I and II did not dissolve in chloroform any more, but formed gel. The observed phenomenon can be explained by the crosslinking of polymer chains caused by an interaction of tertiary amino groups with air or peroxide oxygen, or with halogen-containing solvents.^{11,12}

No changes in the size and mass of the membranes occurred if the latter were placed in variously concentrated water–ethanol solutions.

Pervaporation of EtOH/H₂O through Styrene-Substituted *N*-Phenylmaleimide Copolymer Membranes

The membranes were characterized by the permeate flux J and the separation factor $\alpha_{\text{H}_2\text{O}}$ which was related to the preferentially permeating water. The separation factor is defined by Eq. (1):

$$\alpha_{\text{H}_2\text{O}} = \frac{w_{\text{H}_2\text{O}}^{\text{P}} w_{\text{EtOH}}^{\text{F}}}{w_{\text{EtOH}}^{\text{P}} w_{\text{H}_2\text{O}}^{\text{F}}} \quad (1)$$

where w is the mass fraction of H₂O and EtOH in the permeate (P) and feed solution (F). The results of pervaporation experiments are summarized in Table I.

In the pervaporation all membranes showed an increase in the separation factor $\alpha_{\text{H}_2\text{O}}$ with increasing amount of ethanol in the feed solution. The increase

Table I Pervaporation^a of EtOH/H₂O Mixtures through Membranes Made from Copolymers Styrene-Substituted *N*-Phenylmaleimide at 35°C

Copolymer ^b	[η] ^c (mL g ⁻¹)	w_{EtOH}^F (%)	w_{EtOH}^P (%)	J (g ⁻² h ⁻¹)	$\alpha_{\text{H}_2\text{O}}$
S-I (7.9)	90.6	58.0	11.4	10	10.7
		75.0	6.0	13	47
		83.4	6.9	13	67.8
S-II (7.1)	104.6	65.0	13.8	10	11.6
		75.3	9.2	13	30.1
		84.2	11.3	10	41.8
S-III (4.1)	83.0	59.9	7.2	11	19.3
		85.1	11.6	9	43.5
S-IV (4.5)	72.7	58.6	7.2	16	18.2
		84.4	10.5	13	46.1
S-V (6.1)	81.4	55.7	10.4	9	10.8
		64.2	8.5	8	19.3
		79.8	7.1	9	51.7
S-VI (4.8)	77.0	56.9	9.3	9	12.9
		81.4	12.2	8	31.5

^a w_{EtOH}^F , w_{EtOH}^P , weight fractions of EtOH in the feed solution (*F*) and permeate (*P*), J = permeate flux, $\alpha_{\text{H}_2\text{O}}$ = separation factor related to water.

^b In brackets, mol % of the respective *N*-phenylmaleimide.

^c In benzene at 20°C.

in $\alpha_{\text{H}_2\text{O}}$ was particularly pronounced in the case of membranes with incorporated imides I, V, and II. The separation factor values at 65 and 85 wt % EtOH in the feed solution are, respectively, 23 and 73 for the poly(S-co-I), 21 and 63 for the poly(S-co-V), and 12 and 45 for the poly(S-co-II) membrane. The separation factors of the other membranes obtained in the separation of EtOH/H₂O mixtures containing > 80 wt % EtOH were higher than 40 [poly(S-co-III), poly(S-co-IV)] or 30 [poly(S-co-VI)]. The permeate flux through membranes made from poly(S-co-I) and poly(S-co-II) was 10–13 g m⁻² h⁻¹, the flux through membranes containing halogenated imide structural units was about 9 g m⁻² h⁻¹. The membrane made from poly(S-co-IV) with the flux of the permeate 13–16 g m⁻² h⁻¹ was an exception. The flux values obtained in the measurements suggest a considerable hydrophobicity of the tested membranes.

Compared with membranes made from copolymers of styrene with *N*-phenylmaleimides I–VI, the behavior of those described by Yoshikawa et al.⁴ containing unsubstituted *N*-phenylmaleimide was different in the separation of water-ethanolic solutions. In these membranes, the separation factor $\alpha_{\text{H}_2\text{O}}$ reached its maximum at 50 wt % EtOH in the feed solution and did not exceed 20. An EtOH content in the mixture undergoing separation higher than 50 wt % resulted in impaired separation prop-

erties, which was reflected in a steep decrease in $\alpha_{\text{H}_2\text{O}}$ and an increased flux of the permeate. The authors attributed this phenomenon to swelling of the membranes with ethanol. Contrary to this, membranes containing substituted *N*-phenylmaleimides proved to be suitable particularly in the separation of strongly concentrated EtOH solutions.

The differences observed in pervaporation characteristics should be evaluated bearing in mind the complex character of the separation process, which involves physico-chemical interactions between the membrane material and components of the mixture under separation, i.e., selective sorption, diffusion, and desorption of molecules. It may be assumed that substituents on the phenyl ring of incorporated *N*-phenylmaleimide units influence by their inductive effect the reactivity of carbonyl groups operative as carriers in the preferential water transport,⁴ which also leads to a change in the separation efficiency. Depending on the type and number of substituents in the molecule of *N*-phenylmaleimide, the order (morphology) of the chains may vary along with the chain length, thus causing a change in the pervaporation through the polymeric membranes. Moreover, in the case of membranes made from poly(S-co-I) and poly(S-co-II) containing tertiary amino groups, the formation of a crosslinked structure due to the interaction between amino groups and air oxygen or halogenated solvent is also reflected in the

resulting behavior. Pervaporation characteristics of the tested polymeric membranes are a result of the effect of all these factors. Their role, however, is also dependent on the amount of incorporated imide units.

CONCLUSIONS

Pervaporation of aqueous ethanolic solutions through synthetic membranes made from copolymers of styrene and *N*-phenylmaleimides substituted in the ring with the dimethylamino group (I, II), bromine (III, IV), and chlorine (V, VI) is characterized by a rise in permselectivity with respect to water with increasing concentration of ethanol in the feed solution. The highest separation factor $\alpha_{\text{H}_2\text{O}}$ was obtained with a poly[styrene-co-*N*-(3-dimethylaminophenyl) maleimide] membrane ($\alpha_{\text{H}_2\text{O}} = 73$ at 85 wt % EtOH, 35°C). The average permeate flux was $10 \text{ g m}^{-2} \text{ h}^{-1}$. The resulting pervaporation properties depend on the type and number of substituents in the incorporated *N*-phenylmaleimide monomeric units and on their content in the membrane.

The authors thank Dr. J. Schauer for the kind supply of the apparatus for pervaporation experiments.

REFERENCES

1. B. D. Gupta and A. K. Mukherjee, *Polym., Plast. Technol. Eng.*, **29**, 299 (1990).
2. I. Frennsson, G. Trägårdh, and B. Hahn-Hägerdal, *Chem. Eng. Commun.*, **45**, 277 (1986).
3. Q. T. Nguyen, A. Maazouz, and J. Néel, in *Synthetic Polymeric Membranes*, B. Sedláček and J. Kahovec, Eds., Walter de Gruyter, Berlin-New York, 1987, p. 495.
4. M. Yoshikawa, H. Yokoi, K. Sanui, and N. Ogata, *Polym. J.*, **17**, 363 (1985).
5. M. P. Cava, A. A. Deana, K. Muth, and M. J. Mitchell, *Org. Synth. Coll.*, Vol. V, 944 (1973).
6. F. Hrabák, J. Lokaj, J. Bílá, H. Pivcová, M. Tkaczyk, and J. Biroš, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 267 (1988).
7. V. Hynková and F. Hrabák, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 2587 (1976).
8. J. Lokaj and J. Bílá, *Acta Polym.*, **43**, 54 (1992).
9. J. Lokaj and F. Hrabák, *Eur. Polym. J.*, **14**, 1039 (1978).
10. K. Bouchal, M. Ryska, and F. Hrabák, *Makromol. Chem.*, **178**, 55 (1977).
11. M. Bezděk, V. Hynková, K. Bouchal, and F. Hrabák, *Eur. Polym. J.*, **8**, 1333 (1972).
12. V. Hynková, J. Lokaj, and F. Hrabák, *Makromol. Chem.*, **161**, 285 (1972).

Received November 13, 1991

Accepted February 11, 1992