Pervaporation through Membranes Made from Acyl Derivatives of Poly(2,6-dimethyl-1,4-phenylene Oxide)

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SYNOPSIS

Several acyl derivatives of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were obtained by Friedel–Crafts acylation, and the products were used to prepare membranes. During the pervaporation of 10% aqueous solutions of ethanol, acetone, 1-propanol, or dioxan, membranes made from unmodified, benzoylated, or propionylated PPO (glassy polymers, T_g > 200°C) were preferentially permeable to water, and their separation factors were mainly dependent on the molecular weight of the solvent. Membranes made from palmitoylated PPO (nonglassy polymer, T_g = 34.9°C) were preferentially permeable to organic solvents, and their separation factors correlated with the solubility parameters of the solvents under investigation. As regards membranes made from caproylated PPO (T_g = 130.6°C), there was no unambiguous relation to molecular weights of the solvents or to their solubility parameters. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation is a membrane separation process that combines the evaporation of volatile components of a liquid mixture with their permeation through a selective membrane. It is generally accepted that mass transport through a polymer pervaporation membrane is determined by a solution–diffusion mechanism.[1] As the polymer has influence on both the selective sorption and the selective diffusion of the components of the mixture through the membrane, the choice of the polymer is of prime importance.

Most applications of pervaporation are concerned with the separation of binary mixtures of water–organic solvent, especially ethanol.[2] While in the great majority of polymers water permeates preferentially, only a few membranes are ethanol-permselective; the latter include silicone-based membranes,[3] membranes from poly[1-(trimethyl-silyl)-1-propyne] and some other substituted polyacetylenes,[4] membranes from polymers with fluoroalkyl groups,[5] and from copolymers of styrene with some hydrophobic methacrylic esters.[6] For

practical purposes this choice of membranes should be extended.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an attractive material for the preparation of membranes because it possesses excellent mechanical properties both at room and at elevated temperatures and is also resistant against a number of chemical agents. It is known that with pervaporation membranes from unmodified PPO, water permeates preferentially when used to separate water–ethanol mixtures.[7] In our investigations membranes from acylated PPO were used to demonstrate how the substituent can change the selectivity of the pervaporation membrane.

EXPERIMENTAL

Modification of the Polymer

To a solution of 12.0 g (0.1 mol) of poly(2,6-dimethyl-1,4-phenylene oxide) (Research Institute of Macromolecular Chemistry, Brno, Czechoslovakia, molecular weight M_w = 385,000, measured by light scattering) in 160 mL of 1,2-dichloroethane (40°C), a mixture of the acylating agent (acetyl chloride, propionyl chloride, caproyl chloride, palmitoyl chloride, benzoyl chloride, or acetanhydride, all Fluka

products, purum) and anhydrous aluminum chloride (Fluka, purissimum), also dissolved in 160 mL of 1,2-dichloroethane, was added. After that, the mixture was stirred for another 30 min (if not mentioned otherwise). The acylated polymer was isolated by precipitation into methanol in excess and repurified by repeated precipitation into methanol in excess, with the exception of polymers prepared by a reaction with acetyl chloride or acetanhydride, which were crosslinked during the reaction. The effect of the amount of acyl chloride, $AlCl_3$, and the reaction time on the degree of substitution (acylation) of PPO can be seen in Figure 1 and Tables I and II. (Monoacylation of each phenylene ring represents D.S., degree of substitution, 100%.)

The degree of acylation was determined by comparison using ^{1}H-NMR spectra recorded with a Bruker AC 300 apparatus in $CDCl_3$ (Table IV).

The glass transition temperatures, T_g, were recorded with a differential scanning calorimeter Perkin-Elmer Series 7 (Table IV).

Membrane Preparation

Membranes were prepared by casting the polymers from (5%) chloroform solutions. Polymer solutions
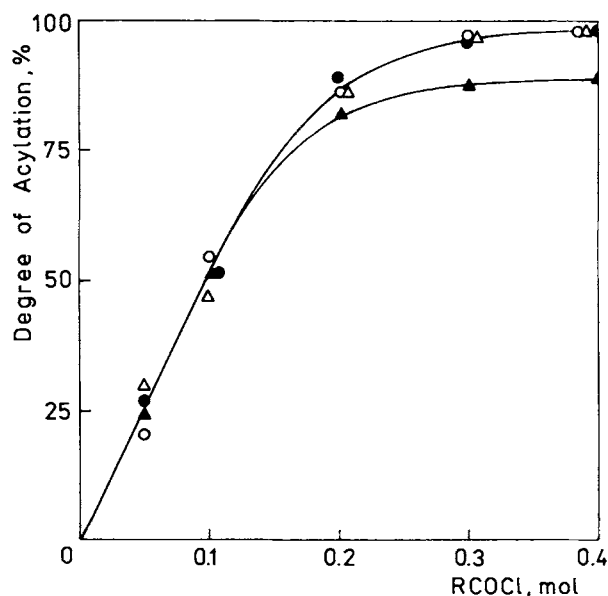
Table I Effect of the Amount of $AlCl_3$ on the Degree of Benzoylation of PPO

Composition of the Reaction Mixture (mol)			Degree of Benzoylation (%)
PPO	$AlCl_3$	Benzoyl Chloride	
0.1	0.0025	0.25	Negligible
0.1	0.01	0.25	4
0.1	0.05	0.25	25

were poured onto a glass plate and spread out with a casting knife. The solvent was evaporated slowly at room temperature over a few days. The membranes used in pervaporation experiments were homogeneous films 20 ± 2 μm thick. The exception was the membrane prepared from palmitoylated PPO, which had insufficient mechanical strength. Therefore a composite membrane was used: The ultrafiltration polysulfone membrane (permeability to water 400 L/m^2 h, cutoff 500,000) was dried, and then contacted from the skin side with a 5% solution of palmitoylated PPO in heptane and dried again.

Pervaporation Experiments

The pervaporation apparatus consisted of a pervaporation cell with a membrane area of 43 cm^2 and a glass apparatus equipped with traps cooled by liquid nitrogen to condense the pervaporate. The feed solution was circulated between the thermostatted bath (250 mL) and the upstream side of the membrane in the cell. The feed temperature was 35°C and the downstream pressure was kept at 400 Pa. The composition of the feed and of the permeate was determined by refractive index measurements using calibration curves.

Figure 1 Effect of the amount of acyl chloride on the degree of acylation of PPO (PPO 0.1 mol, molar ratio $AlCl_3$/acyl chloride 1 : 1); (▲) benzoyl chloride, (○) propionyl chloride, (●) caproyl chloride, (△) palmitoyl chloride. One acyl group on each aromatic ring of PPO corresponds to a 100% degree of acylation.

Table II Effect of Reaction Time on Degree of Benzoylation of PPO[a]

Time of Reaction (h)	Degree of Benzoylation (%)
0.5	51
4.0	53
16.0	55
48.0	55

[a] Mole ratio PPO–benzoyl chloride–$AlCl_3$ 1 : 1 : 1.

The performance of membranes in pervaporation was evaluated by the separation factor and the total flux. The separation factor, α_s^w, is defined as:

$$\alpha_s^w = \frac{x_w^p / x_s^p}{x_w^f / x_s^f} \qquad (1)$$

where x is the weight fraction, the superscripts p and f stand for permeate and feed, respectively, and the subscripts s and w for organic solvent and water, respectively. The total flux J at a steady state (measured approx. after 4 h from the start of the process) was obtained by
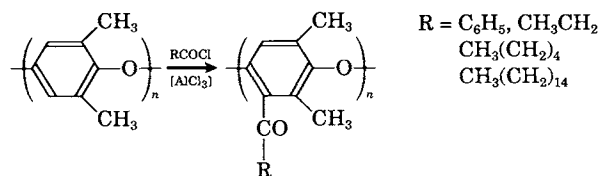
$$J = \frac{Q}{A \times t} \qquad (2)$$

where Q is the total amount permeated during experimental time interval t, and A is the effective surface area.

RESULTS AND DISCUSSION

Modification of Polymers

Since the aromatic ring of PPO is activated with two methyl groups and two ether oxygen atoms, the

Friedel–Crafts acylation of PPO proceeds very easily:

In spite of the activation of the aromatic ring, the second acyl group present in the ring cannot be proved by using ^{1}H-NMR spectroscopy. As expected,[9] the degree of acylation depends on the concentration of aluminum chloride (Table I) and is almost independent of the reaction time (Table II). With the aluminum chloride in excess PPO can be acylated almost quantitatively (Fig. 1), i.e., one acyl group can be introduced into the aromatic ring. Acylation with both acetyl chloride and acetanhydride has always been accompanied by crosslinking of the products. All the other acylated polymers prepared in this study were soluble within a broader range of solvents than unmodified PPO (Table III). While PPO, benzoylated PPO, and PPO containing a short aliphatic substituent are polymers with a high glass transition temperature, the glass transition tem-

Table III   Solubilities of Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and Its Acyl Derivatives (25°)[a]

	δ^b	PPO	Benzoyl PPO[c]	Propionyl PPO[d]	Caproyl PPO[d]	Palmitoyl PPO[d]
Hexane	14.9	I	I	I	I	S[e]
Diethyl ether	15.1	I	I	I	S	S[e]
Cyclohexane	16.8	I	I	I	S	S[e]
Butyl acetate	17.4	I	I	I	S	S[e]
Toluene	18.2	S	S	S	S	S
Chloroform	19.0	S	S	S	S	S
Methyl ethyl ketone	19.0	I	S	S	S	S[e]
Acetone	20.3	I	S[e]	S	S	I
Cyclohexanone	20.3	I	S	S	S	I
Dioxane	20.5	I	S	S	S	I
2-Methyl-1-propanol	21.7	I	I	I	S	I
1-Butanol	23.3	I	I	I	I	I
1-Propanol	24.3	I	I	I	I	I
Dimethylformamide	24.8	I	S	S	S	I
Ethanol	26.0	I	I	I	I	I
Water	47.9	I	I	I	I	I

[a] I = insoluble, S = soluble.
[b] Solubility parameter in $(\text{MPa})^{1/2}$, Ref. 8.
[c] D.S. 88%.
[d] D.S. 98%.
[e] Turbidity.

Table IV Glass Transition Temperatures and ^{1}H-NMR Chemical Shifts of Poly(2,6-dimethyl-1,4-phenylene oxide) and Its Acyl Derivatives

Polymer	T_g (°C)	δ (ppm)
PPO	213.0	2.0, 6.4
Benzoyl PPO (D.S. 88%)	238.9	2.0, 6.05, 6.4, 7.4, 7.8
Propionyl PPO (D.S. 98%)	225.8	1.1, 2.0, 2.9, 6.05, 6.4
Caproyl PPO (D.S. 98%)	130.6	0.8, 1.3, 1.7, 2.0, 2.9, 6.05, 6.4
Palmitoyl PPO (D.S. 98%)	34.9	0.8, 1.3, 1.7, 2.0, 2.9, 6.05, 6.4

perature decreases with increasing length of the substituent (Table IV).

Pervaporation Properties

As pervaporation is a process that combines the evaporation of volatile components of a mixture with their permeation through a membrane by a solution–diffusion mechanism, separation factor values depend on the following three factors concerning the nature of the organic liquid: affinity to the membrane, bulkiness of the molecule, and vapor pressure. These factors correlate with the solution, diffusion, and vaporization, respectively. In particular cases various factors may assume the predominant role. During the pervaporation of 10% aqueous solutions of some selected organic solvents, membranes made from unmodified PPO, benzoylated PPO, and propionylated PPO were preferentially permeable to water (Table V). All these polymers are in the glassy state and have the glass transition temperature above 200°C (Table IV). In the case of membranes

made from unmodified PPO the separation factor α_s^w increases in the order ethanol < acetone < 1-propanol < dioxan, i.e., with increasing molecular weight of the solvent. Here, we assume that the factor that affects the separation predominantly is the size of the permeated molecule. The order observed with benzoylated and propionylated PPO is similar, only the separation factor α_s^w is lower for acetone than for ethanol. In the case of acetone, which has a low boiling point, upstream vapor pressure has also a pronounced effect. On the contrary, membranes made from palmitoylated PPO, a nonglassy polymer ($T_g = 34.9$°C), are preferentially permeable to organic solvents. The separation factor increases in the series ethanol > propanol > dioxan > acetone, i.e., in the order of values of their solubility parameters. In this case we assume that the predominant factor is affinity of the solvent toward the material of the membrane. As regards membranes made from caproylated PPO (T_g is intermediate, 130.6°C), the order of the separation factors is not correlated unambiguously with the order of molecular weights or

Table V Pervaporation of 10% Aqueous Solutions of Organic Solvents Through Homogeneous Membranes[a]

Polymer	Ethanol		Acetone		1-Propanol		Dioxane	
	J[b]	$\alpha_s^{w\,c}$	J[b]	$\alpha_s^{w\,c}$	J[b]	$\alpha_s^{w\,c}$	J[b]	$\alpha_s^{w\,c}$
PPO	23	6.3	23	6.4	22	13.7	21	720
Benzoyl PPO (D.S. 88%)	180	1.6	170	1.0	147	1.8	133	2.6
Propionyl PPO (D.S. 98%)	110	3.3	18	1.1	90	8.9	80	50
Caproyl PPO (D.S. 98%)	22	4.6	28	0.59	20	6.2	24	2.2
Palmitoyl PPO[d] (D.S. 98%)	60	0.50	170	0.11	90	0.37	100	0.30

[a] Thickness 20 μm.
[b] Total flux defined in eq. (2), g/m^2 h.
[c] Separation factor defined in eq. (1).
[d] Composite membrane.

with the order of the solubility parameters of the solvents, and the size of the molecule of the solvent and its affinity to the material of the membrane are not the predominant factor in this case.

Membranes made from benzoylated and propionylated PPO have much higher fluxes than those made from unmodified PPO. The higher packing density of modified PPO caused by bulky substituents is obviously reflected in this case.[10]

CONCLUSIONS

During the pervaporation of aqueous solutions of organic solvents, membranes made from unmodified poly(2,6-dimethyl-1,4-phenylene oxide) and from its acyl derivatives, having a high glass transition temperature, are preferentially permeable to water. Introduction of long side chains into the PPO molecule reduces the glass transition temperature. At a sufficiently reduced glass transition temperature (palmitoylated PPO, $T_g = 34.9°C$) the membranes are preferentially permeable to organic solvents.

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