

Effect of Molecular Weight Parameters on Gas Transport Properties of Poly(2,6-dimethyl-1,4-phenylene oxide)

G. A. POLOTSKAYA,* S. A. AGRANOVA, N. V. GAZDINA, YU. P. KUZNETSOV, and V. V. NESTEROV

Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoy Prospect 31, St. Petersburg 199004, Russia

SYNOPSIS

The gas permeability of O₂ and N₂ for homogeneous and composite membranes prepared from poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) samples with different molecular weight parameters was investigated. Temperature dependencies of gas permeability coefficients and permselectivity were determined for homogeneous membranes. It was established that gas permeability coefficients of homogeneous membranes depend on molecular weight of the polymers used. The gas permeability of composite membranes with a PPO selective layer was investigated as a function of PPO intrinsic viscosity [η] and its casting solution concentration (*c*). It was shown that under the condition [η] · *c* = const it is possible to obtain composite membranes with the same transport properties by using polymers with different molecular weight parameters. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The chemical structure and molecular weight parameters are the most important characteristics of polymers that may determine transport properties of polymer membranes. In recent years the relationship between the chemical structure and transport properties of polymers used for the preparation of gas separating membranes has been widely investigated.¹⁻³

The problem of the effect of polymer molecular weight parameters on the gas transport properties of membranes has not been studied in sufficient detail, although it may be very important for improving the performance of synthetic polymer membranes. Some researchers were of the opinion^{4,5} that after attaining MW 10⁴–2 × 10⁴ the gas permeability coefficients become constant by analogy with other physical–mechanical properties of polymers, and subsequently do not depend on MW. However, more recent data indicate that this dependence exists.⁶ In our preceding work⁷ for a composite membrane with a polyetherimide

top layer it has been shown that with increasing MW from 7.2 × 10³ to 1.3 × 10⁴, the diffusion coefficient of argon decreases markedly. Upon further MW increase to 2.2 × 10⁴ there is a tendency to a slight increase in this coefficient. Unfortunately, peculiar features of polyetherimide synthesis do not make it possible to prepare and to study the higher molecular weight polymer.

The purpose of the present work was to study the effect of MW parameters (over a wide MW range) on gas separating properties of homogeneous and composite membranes. The polymer investigated was poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). It is known to be one of the most permeable glassy polymers. The mechanism of gas transport in PPO homogeneous membranes has been investigated, and the possibility of varying its gas transport properties during chemical modification has been shown.⁸⁻¹³ Smid and coworkers have reported the influence of PPO MW on the formation of asymmetric hollow fibers and their gas separating properties.¹⁴ They have shown that the increase in the polymer MW makes it possible to produce membranes with higher permeability, whereas the selectivity remains the same.

In the present work plane composite and homogeneous membranes were studied by passing air (O₂

* To whom correspondence should be addressed.

Table I Some Physical Properties of PPO Samples

| Samples (<i>N</i>) | $[\eta]$ (dL/g) | $M_w \cdot 10^3$ | M_w/M_n | ρ (g/cm ³) | V_f (cm ³ /g) |
|-------------------------|--------------------|------------------|-----------|--------------------------------|-------------------------------|
| PPO-1 | 0.68 | 70.1 | 3.40 | 1.0699 | 0.1697 |
| PPO-2 | 0.87 | 100.1 | 3.83 | 1.0687 | 0.1707 |
| PPO-3 | 0.96 | 171.9 | 4.74 | 1.0671 | 0.1721 |
| PPO-4 | 1.58 | 357.9 | 6.70 | 1.0680 | 0.1713 |

and N₂ mixture) through them, and established specific features supplement foregoing data.

EXPERIMENTAL

PPO samples with intrinsic viscosity $[\eta]$ of 0.68, 0.87, 0.96, and 1.58 dL/g (PPO-1, PPO-2, PPO-3, and PPO-4, respectively) were used for membrane preparation. The $[\eta]$ value of PPO was determined with a Ubbelohde viscometer in chloroform at 25°C.

Size exclusion chromatography (SEC) was carried out on a standard chromatograph with refractometric and spectrophotometric detection by using a system of microstyrigel columns (10⁴ Å, 10⁵ Å, and 10⁶ Å) in chloroform. This chromatographic system met all the requirements of SEC, its efficiency was 21 × 10³ plates, and separation selectivity was ensured in the MW range from 2 × 10³ to 2 × 10⁶ Da. The molecular characteristics of PPO samples were calculated by using universal calibration and a special computer program.

Homogeneous membranes (100–120 μm thick) were obtained by casting a 5–12 g/dL PPO solution in chloroform on cellophane with subsequent drying to constant weight.

Composite membranes were prepared by casting 1–12 g/dL PPO solution in chloroform on the surface of ultrafiltration polysulfoneamide membrane (UPM) as a standard support. Excess solution was poured off, and the membrane was dried in the vertical position.

The density (ρ) of PPO samples was determined at 25°C by the flotation method using an aqueous solution of saccharose. The same homogeneous PPO membranes which were investigated for gas permeability were used for density measurements.

The free volume was calculated by a known procedure: $V_f = V_{sp} - 1.3 \times V_w$, where $V_{sp} = 1/\rho$ is the specific volume and V_w is the Van der Waals volume calculated by Bondy's method.

Gas permeability parameters were measured on a PGD-01 gas chromatography installation with the

aid of a diffusion type cell at 30–100°C and a partial pressure of 1 bar.

RESULTS AND DISCUSSION

Homogeneous Membranes

Table I lists some physical properties of the PPO samples used in this work. The molecular weight of these samples increases in the following series: PPO-1 < PPO-2 < PPO-3 < PPO-4. Gas transport properties were investigated for homogeneous membranes prepared from PPO-1-4. Figure 2 shows the temperature dependencies of O₂ and N₂ permeability coefficients (P) and the selectivity of their separation. For all membranes $P(O_2)$ and $P(N_2)$ increase with temperature and with a simultaneous decrease in the permselectivity from 4.3 to 3.0. Moreover, at a fixed temperature the value of permselectivity is virtually independent of the PPO molecular weight.

For each temperature $P(O_2)$ and $P(N_2)$ increase in the following series: PPO-1 < PPO-2 < PPO-3. In other words, permeability improves with the polymer MW. An analogous correlation has been obtained in investigation of hollow fiber PPO membranes.¹⁴

In order to establish the physical meaning of this correlation, the values of MW, density, and free volume were compared. The data in Table I show that the density of PPO-1-3 films reduces with increasing MW. The reduction of density leads to an increase in free volume, which evidently favors an increase in permeability.

It is noteworthy that the temperature dependence of $P(O_2)$ and $P(N_2)$ for membrane from PPO-4 with the highest MW is anomalously situated in the plot (Fig. 1, curves 4 and 4'). One of the possible reasons is the higher polydispersity (M_w/M_n) of the PPO-4 sample, which contains a greater amount of low MW fractions than PPO-1-3. It has been reported¹⁵ that macromolecules with lower MW exhibit higher mobility in solution and form a more organized and denser structure in the condensed state. A denser

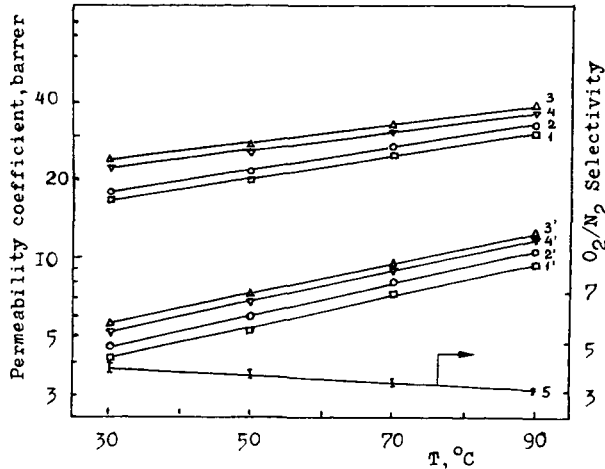


Figure 1 Temperature dependence of the O₂ (curves 1-4) and N₂ (curves 1'-4') permeability coefficients and the O₂-N₂ permselectivity (curves 5) for homogeneous membranes prepared from PPO-1-4 with different MW.

structure is more resistant to gas transport. Therefore, the increase in M_w/M_n may be regarded as a factor decreasing the gas permeability coefficients. In order to establish in detail the role of polydispersity, similar investigations must be carried out for a wide range of samples with different polydispersities.

We believe that polymer MW and polydispersity should be taken into account as additional factors in the study of gas permeability properties.

Composite Membranes

It was of interest to investigate the effect of MW parameters on the gas separating properties of composite membranes with a thin selective PPO layer on the surface of a standard polymer support because the supermolecular structure of this layer can differ from that of a homogeneous membrane.

The characteristics of the casting solution for the formation of a surface layer determine to a certain extent the gas separating properties of a composite membrane. The effect of casting solution concentration on the transport properties of composite membranes has been reported.¹⁶ We observed that the intrinsic viscosity ($[\eta]$) of the polymer should also be taken into account. In this connection the influence of casting solution concentration on O₂ and N₂ permeability was studied for composite membranes prepared by using three PPO samples (PPO-1, 3, and 4), with different $[\eta]$ values: 0.68, 0.96, and 1.58 dL/g.

It can be seen from Figure 2 (curves 1-3 and 1'-3') that in all cases the increase in the initial con-

centration (c) of PPO casting solution leads to a decrease in composite membrane permeability. A more detailed analysis shows that for all membranes the same permeability is attained by using casting solutions obeying the condition $[\eta] \times c = \text{const}$ (Fig. 2, straight lines A-D for O₂ and A'-D' for N₂).

It is known that the $[\eta] \times c$ product characterizes the volume fraction of the macromolecules and the degree of their interaction with each other and with the solvent.¹⁷ In dilute solutions at $[\eta] \times c < 1$ the interaction between macromolecules is virtually absent. In more concentrated solutions at $[\eta] \times c > 1$ the interactions between macromolecules appear to lead to chain entanglement and network formation.

It would be natural to assume that an increase in the $[\eta] \times c$ value causes the formation of a denser network in solution and a decrease in permeability of corresponding membranes. This assumption was verified by experiment. Figure 3 shows the dependence of composite membrane permeability on $[\eta] \times c$ value. The use of PPO solutions with $[\eta] \times c > 8$ forms membranes with low permeability. Whereas the casting solutions at $[\eta] \times c < 2$ are used, defective layers are formed, which is verified by a decrease in permselectivity. At the same time membranes formed from a casting solution with $[\eta] \times c = 3 \div 4$ have an optimum combination of permeability and permselectivity.

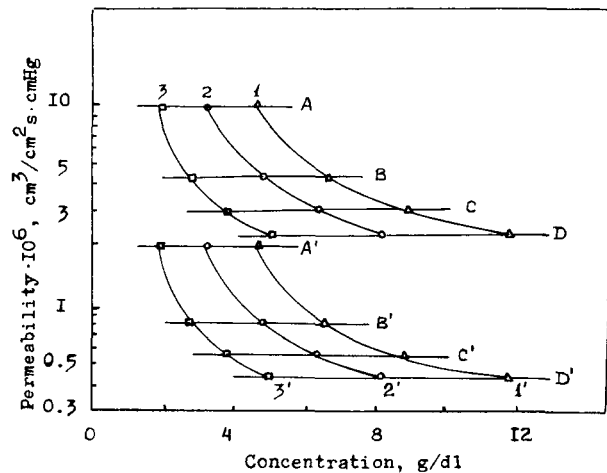


Figure 2 Composite membrane permeability of O₂ (curves 1-3) and N₂ (curves 1'-3') versus concentration of PPO casting solution. $T = 30^\circ\text{C}$.

Curves 1 and 1' = PPO-1 with $[\eta] = 0.68$ dL/g
 2 and 2' = PPO-3 with $[\eta] = 0.96$ dL/g
 3 and 3' = PPO-4 with $[\eta] = 1.58$ dL/g

Straight lines A and A' $[\eta] \times c = 3.0$
 B and B' $[\eta] \times c = 4.5$
 C and C' $[\eta] \times c = 6.0$
 D and D' $[\eta] \times c = 8.0$

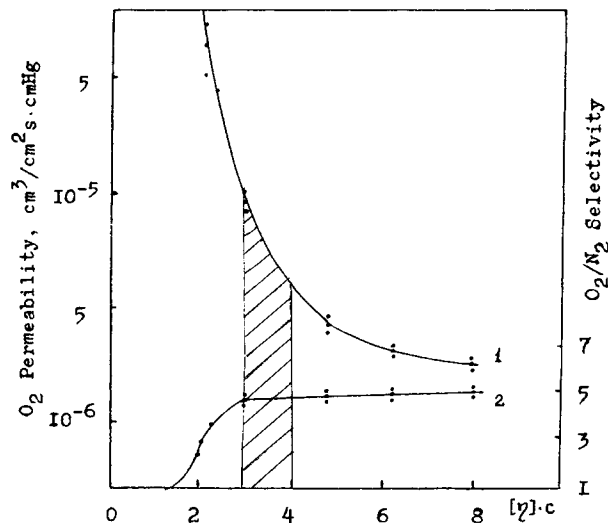


Figure 3 The O_2 permeability (1) and the O_2/N_2 permselectivity (2) of composite membranes versus the $[\eta] \times c$ value of PPO casting solution.

Hence, the $[\eta] \times c$ product may be considered to be a universal parameter determining the transport properties of composite membranes in the stage of surface layer formation.

It should be noted that for composite membranes the anomalous gas permeability of PPO-4 samples was not observed. The effect of high polydispersity which determines the denser structure of the homogeneous membrane does not evidently exist under the conditions of casting a thin top layer of composite membranes. In this case the top layer is formed during short contact of the casting solution with the support. Rapid transition of the polymer from solution into the condensed state probably occurs without any disordering of packing macromolecules of different length in the thin top layer.

CONCLUSIONS

It was established for homogeneous membranes that the gas permeability of PPO membranes depends on polymer MW. The molecular polydispersity of the polymer (M_w/M_n) should also be taken into account.

In the investigation of the gas permeability of composite membranes with a PPO top layer, it was

found that a universal dependence of membrane permeability on the volume fraction of the polymer in the casting solution is observed. This dependence is controlled by the $[\eta] \times c$ value. It was shown that under the condition $[\eta] \times c = \text{const}$ it is possible to obtain composite membranes with the same level of permeability by using polymers with different MW.

It may be assumed that this dependence can also be used for the preparation of other types of composite membranes.

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