

# Gas Transport in Lanthanide-Polymer Membranes

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## Synopsis

Permeation properties of O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> were investigated by using copolymer membranes having the pyridine-lanthanide complexes group. The membranes of poly(4-vinylpyridine-co-*n*-butylmethacrylate) and its complexes with lanthanide were prepared. Complexation with lanthanide can be used to tailoring selectivity of CO<sub>2</sub>/O<sub>2</sub>. The CO<sub>2</sub> permeability for pure copolymer is larger than O<sub>2</sub> permeability, but CO<sub>2</sub> permeability is smaller than O<sub>2</sub> permeability for lanthanide-polymer, which is opposite to most polymers. The upstream pressure dependence of gases in lanthanide-polymer varies with temperature. A tentative explanation is given for the results according to the free volume model.

## INTRODUCTION

A gaseous mixture can be separated or enriched by using a polymer membrane because of selective sorption and transport of gases in a polymer membrane. Many efforts have been made to improve the selectivity and the permeation rate.<sup>1</sup> One approach is to modify the structure of the membrane and the interaction of gas with the membrane by addition of metal ions into polymer.<sup>2</sup> The methods of addition of metal ions are: liquid membrane<sup>3</sup>; ion exchange membrane<sup>4</sup>; incorporation of metal complexes<sup>5</sup>; coordination of metal ions to the ligand in polymer chains.<sup>6</sup> We investigated gas transport in lanthanide-polymer membranes with this last membrane system, that is, coordination of rare earth metal ions to the pyridine moiety in poly(4-vinylpyridine-co-*n*-butyl methacrylate) (PBMAVPy).

## EXPERIMENTAL

### Materials

Poly(4-vinylpyridine-co-*n*-butyl methacrylate), with a molar fraction of 4-vinylpyridine of 0.26, was synthesized by the usual radical copolymerization of 4-vinylpyridine and *n*-butyl methacrylate in ethanol initiated by benzoyl peroxide.

### Preparation of Membranes

The lanthanide-PBMAVPy membranes were prepared as follows: lanthanide chloride was dissolved in ethanol and precomplexed with acetylacetone, in order

to prevent the crosslinking of PBMAVPy when mixed together, by delaying the multiple coordinating of metal ions with pyridine ligand. The chloroform solution of a mixture of PBMAVPy and lanthanide chloride was cast on the PTFE plate. After the evaporation of solvent, a pale yellow membrane was obtained. The Ln-PBMAVPy membranes were insoluble in chloroform, which indicated that the metal ions coordinated with two or more pyridine ligands in copolymer chains and caused a crosslinking between polymer chains.

The results of XPS show that the binding energy of N in pyridine increased in Ln-PBMAVPy. The IR absorption of PBMAVPy in  $1600\text{ cm}^{-1}$  shifted to the higher wavelengths. These results confirmed the coordination of metal ions with pyridine ligand in PBMAVPy.

### Permeation Experiment

The gas permeability was measured by an apparatus with a permeation cell which was linked to a gas chromatograph. The diameter of the membrane was 5 cm. The volume of gas permeated per unit time was calculated from the peak area of the GC curve, from which the permeability of gas at standard condition was evaluated.<sup>7</sup> The GC detector was a thermal conductivity cell. The GC column was packed with a 60–80 mesh 5-Å molecular sieve for measuring O<sub>2</sub>, N<sub>2</sub>, and silica for measuring CO<sub>2</sub>.

## RESULTS AND DISCUSSION

Complexation of polymer with a lanthanide may offer a useful technique for tailoring selectivity characteristics of membranes for gas separation. The permeability of CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> in both pure copolymer and Ln-PBMAVPy membranes are presented in Table I. It is noticed that the CO<sub>2</sub> permeability decreased greatly as the lanthanide ions coordinated with PBMAVPy while  $P_{\text{O}_2}$  and  $P_{\text{N}_2}$  only changed slightly. It is interesting that the coordination of lanthanide ions changed  $P_{\text{CO}_2}$  from larger than  $P_{\text{O}_2}$  to smaller than  $P_{\text{O}_2}$ . As a result, the

TABLE I  
Permeability and Selectivity of Lanthanide-PBMAVPy

Metal ion	$P_{\text{O}_2}$	$P_{\text{N}_2}$	$P_{\text{CO}_2}$	$P_{\text{O}_2}/P_{\text{N}_2}$	$P_{\text{CO}_2}/P_{\text{O}_2}$
a	8.5	2.6	23	3.3	2.7
b	11	2.8	30	3.9	2.7
Ce(III)	14	5.1	9.0	3.0	0.66
Nd(III)	9.3	3.1	6.9	3.0	0.74
Gd(III)	9.7	3.4	4.4	2.9	0.45
Dy(III)	6.3	2.2	2.3	2.9	0.37
Er(III)	6.9	2.1	0.86	3.4	0.12
Yb(III)	7.0	2.2	3.1	3.2	0.44
Lu(III)	8.6	2.7	3.5	3.2	0.41

a = PBMAVPy; unit of  $P$ , *barrers*; driving pressure, 1.8 kg/cm<sup>2</sup>.

b = With acetylacetone wt % same as Ln-PBMAVPy; (Ln)/(pyridine) = 3 : 10; temperature: 298 K.

$\text{CO}_2/\text{O}_2$  selectivity was decreased greatly, especially for Erbium ion. The Ln-PBMAVPy gives a  $\text{CO}_2/\text{O}_2$  selectivity opposite to most polymers in published results.<sup>8</sup> To the best of our knowledge, this is the first time the gas permeation properties of Ln-PBMAVPy membrane have been investigated.

The decrease of  $P_{\text{CO}_2}$  and  $\text{CO}_2/\text{O}_2$  selectivity arising from the complexation of Ln with PBMAVPy may be related to the loss in free volume available for solution of gas in the membrane and also a decrease of gas diffusivity in the membrane arising from the coordination of Ln with PBMAVPy and the cross-linking between polymer chains. These result in the decrease of mobility of macromolecular chains and the free volume of polymer. The effect of cross-linking between polymer chains which inhibits polymer segmental motions on

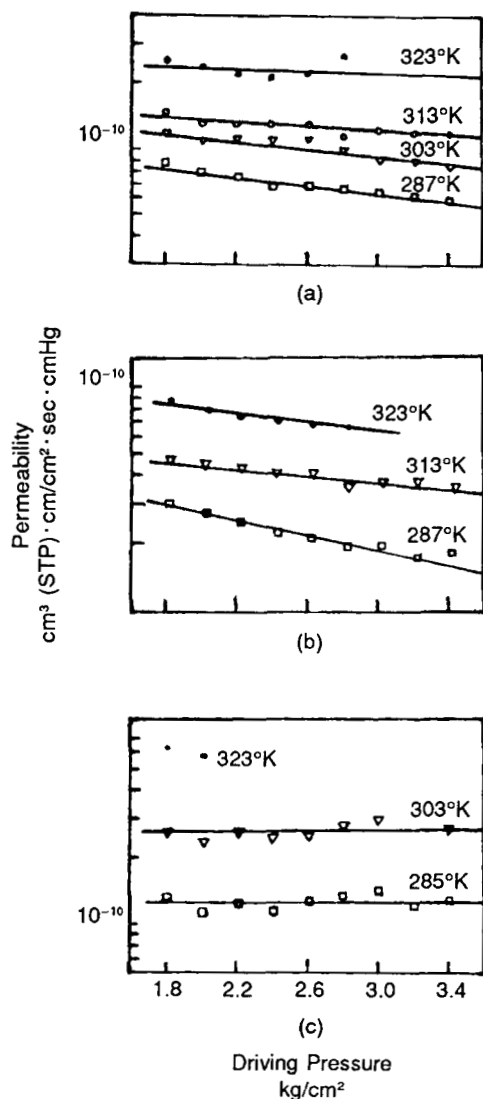


Fig. 1. Dependence of gas permeability in PBMAVPy on driving pressure: (a)  $\text{O}_2$ ; (b)  $\text{N}_2$ ; (c)  $\text{CO}_2$ .

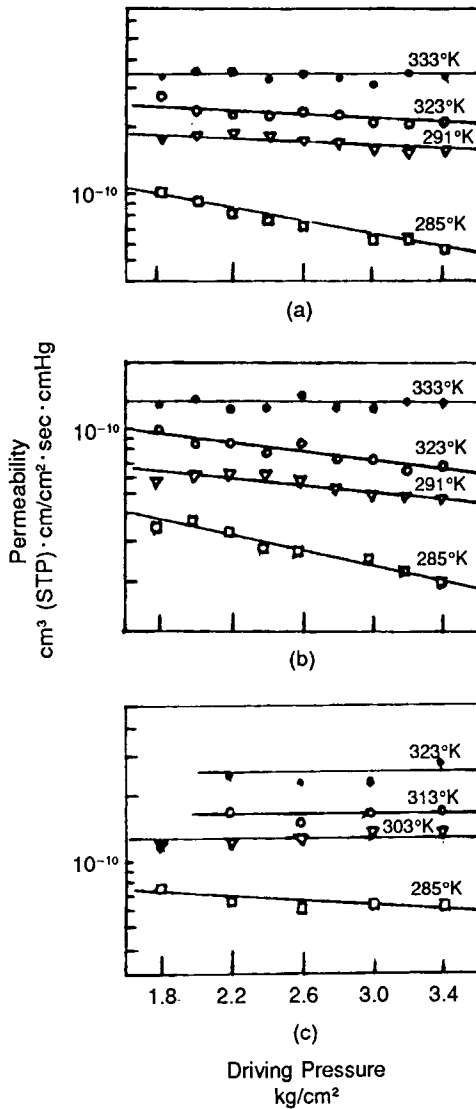


Fig. 2. Gas permeability in  $\text{Ce}^{3+}$ -PBMAVPy as a function of pressure difference: (a)  $\text{O}_2$ ; (b)  $\text{N}_2$ ; (c)  $\text{CO}_2$ .

$P_{\text{CO}_2}$  is even more pronounced than for  $\text{O}_2$ , which leads to a decrease of separation factor for  $\text{CO}_2/\text{O}_2$  as the  $\text{CO}_2$  has a larger size than  $\text{O}_2$ .

The dependence of gas permeability on the driving pressure is shown in Figures 1–4 as a function of temperature. At lower temperatures, the permeability of gas decreased with increasing driving pressure. As the temperature increased, the permeability of gas tends to be independent of the driving pressure.

An increase in the upstream driving pressure may result in two opposing effects: (1) An increase in the concentration of the penetrant dissolved in the polymer film causes an increase in free volume; (2) a rise in the hydrostatic pressure on the high pressure side causes a decrease in the free volume, which

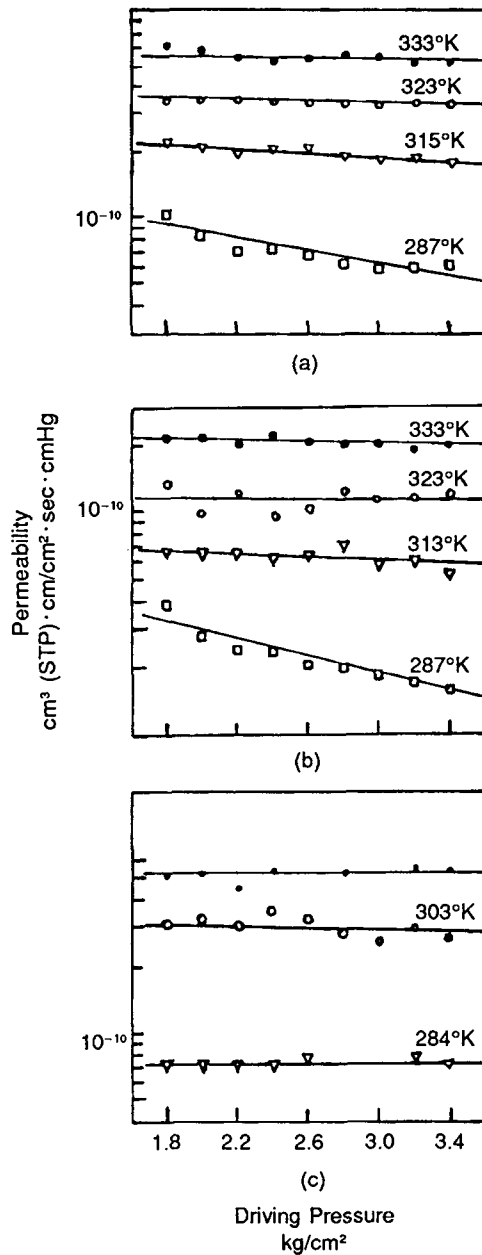


Fig. 3. Gas permeability vs. driving pressure in  $\text{Nd}^{3+}$ -PBMAVPy (a)  $\text{O}_2$ ; (b)  $\text{N}_2$ ; (c)  $\text{CO}_2$ .

would cause a decrease of gas permeability. So the pressure dependence of permeability reflects how the free volume of the polymer is affected by pressure at different temperatures. At lower temperatures, the mobility of macromolecular chains is lower and the decrease of free volume resulting from the rise in driving pressure dominates. At higher temperatures, the segmental motion of macromolecular chains become significant. These factors affecting the free volume, decrease or increase and may offset each other.

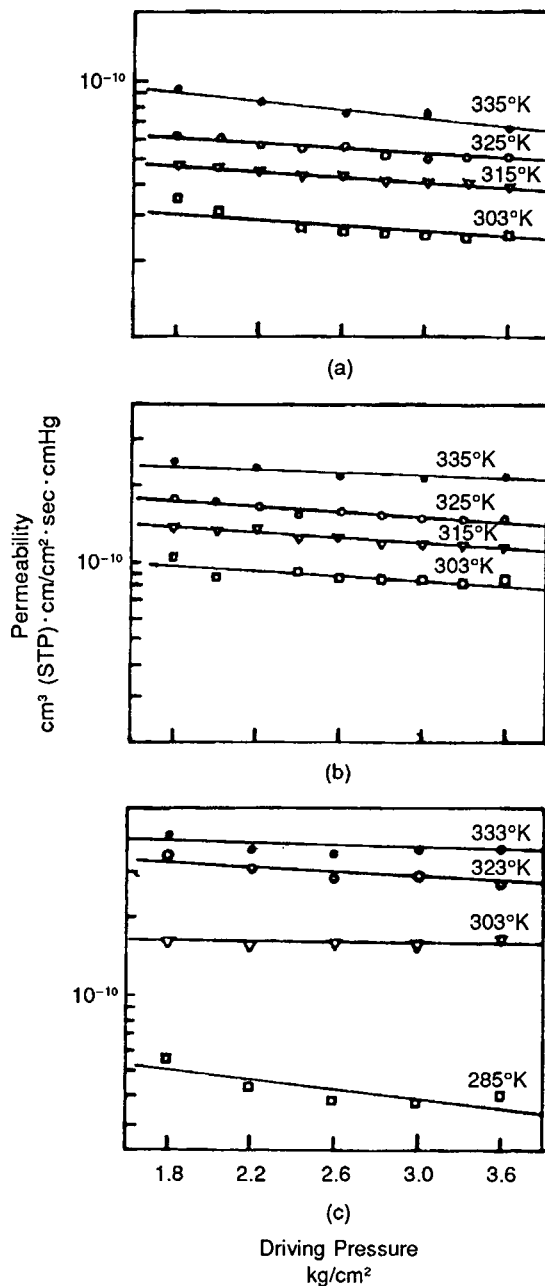


Fig. 4. Relationship of gas permeabilities with driving pressure at different temperature in  $\text{Dy}^{3+}$ -PBMAVPy: (a)  $\text{O}_2$ ; (b)  $\text{N}_2$ ; (c)  $\text{CO}_2$ .

The permeability of gases varied with the change of upstream pressure at lower temperature as shown in Figures 1-4, which suggests that the sorption of gases in the PBMAVPy and Ln-PBMAVPy is dual mode, i.e., Henry's mode solution and Langmuir's mode sorption.<sup>9</sup> The former is independent of upstream pressure and the latter is dependent on upstream pressure. The results of Figures

TABLE II  
Activation Energy of Permeation in Ln-PBMAVPy at Different Pressures<sup>a</sup>

Membrane \ $p$	$E_p$ (O <sub>2</sub> )			$E_p$ (N <sub>2</sub> )			$E_p$ (CO <sub>2</sub> )		
	1.8	2.6	3.4	1.8	2.6	3.4	1.8	2.6	3.4
PBMAVPy	6.9	4.8	3.3	6.4	5.5	3.7	7.9	—	—
Ce <sup>3+</sup>	6.4	6.2	7.2	6.3	6.4	7.1	7.5	5.8	7.2
Dy <sup>3+</sup>	4.7	6.2	6.9	5.5	7.0	—	7.8	5.1	5.1
Nd <sup>3+</sup>	6.2	8.4	8.6	7.1	9.2	11	9.1	9.3	9.5

<sup>a</sup> Unit of  $p$ , kg/cm<sup>2</sup>; unit of  $E_p$ , kcal/mol; temperature: 298 K.

1–4 also indicate that when the temperature increases, the sorption due to the Langmuir mode becomes less and even disappears.

To compare Figure 1 with Figures 2–4, we can see that the coordination of Ln with PBMAVPy improves the durability of the PBMAVPy membrane. The temperature at which the Ln-PBMAVPy membrane can withstand the increase of driving pressure is 10°C or higher than that at which a PBMAVPy membrane fails.

Good linear dependencies of permeability with temperature are observed for the experimental temperature ranges. The permeation activation energy is obtained and the data are given in Table II. The complexation of lanthanide causes a change of pressure dependence of permeation activation energy.

## CONCLUSION

Contrary to PBMAVPy, CO<sub>2</sub> permeability of Ln-PBMAVPy is smaller than O<sub>2</sub>, i.e., the coordination of lanthanide changed the CO<sub>2</sub>/O<sub>2</sub> selectivity from larger than 1 to smaller than 1. There exists a pressure dependence of permeability at lower temperature and as the temperature increases, it tends to disappear.

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