CP-II-6

PERMEABILITY OF METALLOCENIC POLYOLEFINS

María F. Laguna, María L. Cerrada, Rosario Benavente, Ernesto Pérez*
Instituto de Ciencia y Tecnología de Polímeros (CSIC), 28006 Madrid, Spain. Phone: 34-915622900

and Raul Quijada
Dpto. de Ingeniería Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile and Centro de Investigación Interdisciplinaria Avanzada en Ciencias de los Materiales, Santiago, Chile.

INTRODUCTION

The correlation between metallocene structure and polymerization behavior for homo and copolymerization of ethylene and α-olefins has been extensively studied. Bridged metallocene catalysts have shown optimum stereoregularity together with high catalytic activity in the polymerization of olefins[1]. Evidently, the comonomer content will be the primary factor affecting to the final properties of ethylene copolymers and therefore to the transport properties.

In this work the permeation behavior to different gases is studied in two copolymer samples: an ethylene-1-hexene copolymer synthesized by a metallocene catalyst system and a commercial metallocene copolymer of ethylene-1-octene. The characteristics of the films[2,3] are shown in Table I.

Table I. Characteristics of the samples.

Sample	Comonomer Type	content (mol%)	M_w	M_w/M_n	Density (g . cm^{-3})	f_c^{WAXD}	T_m (ºC)
CEH4.2	1-hexene	4.2	108000	2.4	0.9088	0.43	100
CEO5.2	1-octene	5.2	95000	2.5	0.9020	0.40	94

EXPERIMENTAL

Measurements of the permeability were performed using an experimental set-up[4] with two chambers separated by the film. The permeabilities of H_2 , O_2 , N_2 , CH_4 , C_2H_4 and CO_2 in these copolymers have been measured at 1 bar of pressure and 30ºC of temperature. The values of D, S and P for the two membranes and the different gases are presented in Table II.

Table II. Characteristics of the gases studied (critical molar volume, V_c , kinetic diameter, σ_k , and critical temperature, T_c) and results of diffusion, solubility and permeability coefficients[a].

	V_c			CEO5.2			CEH4.2		
Gases	(cm^3/mol)	σ_k (Å)	T_c (K)	D x 10^7	S x 10^5	P	D x 10^7	S x 10^5	P
H_2	65.1	2.89	33.24	125	0.2	25.0	-	-	-
O_2	73.4	3.46	154.58	9.3	0.95	8.8	7.3	0.70	5.1
N_2	89.8	3.64	126.20	8.2	0.46	3.8	5.4	0.37	2.0
CO_2	93.9	3.3	304.21	6.4	3.02	46.9	5.1	1.82	6.2
CH_4	99.2	3.8	191.05	3.9	12.2	11.8	3.4	6.55	11.8
C_2H_4	131	3.9	282.34	2.1	7.3	25.7	1.8	5.31	27.1

[a]D has units of cm^2/s, S (cm^3 of gas(STP) / cm^3 cm Hg) and P (barrers).

RESULTS AND DISCUSSION

The results show that an increase in the size of the penetrant leads to an increase in the solubility and a decrease in the diffusion coefficient. For the two studied membranes, penetrant permeability increases with the critical temperature but there is a notable exception: P of hydrogen is higher than its T_c suggests. This is due to the high value of D that overcomes the rather low solubility of this gas. On the other hand, for the two samples, D follows the trends $D(H_2) > D(O_2) > D(N_2) > D(CO_2) > D(CH_4) > D(C_2H_4)$ and the values of lnD are plotted as a function of the square of the diameter of the diffusants in Figure 1. The values lie fairly well in a straight line except those corresponding to CO_2 that fall far below the regression line.

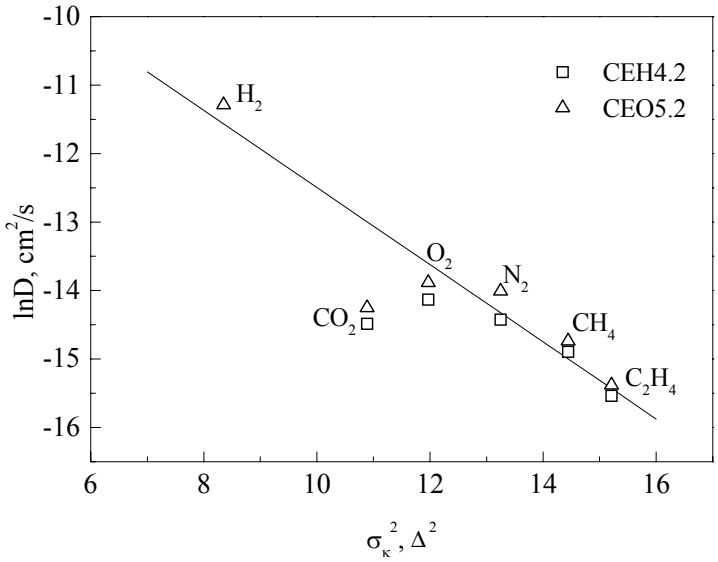

Figure 1. Semilogarithmic plot of D as a function of the kinetic diameter of the gas.

The permselectivity coefficient of CO_2 with respect to oxygen is a very important parameter in films used in the package industry. The results in the present study show that the values of that parameter are very similar for CEO5.2 and CEH4.2: 5.32 and 5.31, respectively.

Acknowledgments:

The financial support of Comunidad de Madrid (Project 07G/0038/2000) and MCT (Project MAT2001-2321) is gratefully acknowledged.

REFERENCES:

(1) Quijada R.; Dupont J.; Lacerda M.; Sciopioni R.; Barrera G. *Macromol. Chem. Phys*. **1995**, *196*, 3991.
(2) Cerrada M.L.; Benavente R.; Peña B.; Pérez E. *Polymer*. **2000**, *41*, 5957.
(3) Cerrada M.L.; Benavente R.; Pérez E. *J. Mater. Res*. **2001**, *16(4),* 1103.
(4) Laguna M.F.; Guzmán J.; Riande E. Polymer **2001**, *42*, 4321.