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Syndiotactic polypropylene copolymer membranes and their performance for oxygen separation

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ABSTRACT

Syndiotactic poly(propylene-α-olefin) copolymers with controlled microstructure and desired properties for oxygen enrichment have been synthesized via metallocene catalysts. The controlled incorporation of comonomers as pendant branch mainly improved the oxygen permeability, but the oxygen/nitrogen selectivity dropped around 20%. By controlling the amount and length of the branches in the syndiotactic polypropylene, the permeability of the membrane was enhanced up to 12-fold and it is comparable to typical commercial polymers used for this application. In contrast with conventional commercial polypropylene, copolymers with a large amount of comonomer were soluble in cyclohexane, allowing the manufacture of composite membranes with high permeance.

1. Introduction

Gas separation technology by membranes has grown rapidly in recent years. Commercial production of oxygen-enriched air was developed in the 1980s and is now one of the main gas separation markets, and the high quality of oxygen can be used in combustion processes (to improve high-temperature furnaces) and medical applications [1]. The production of nitrogen-enriched air is also important in inert gas blanketing of fresh fruits and vegetables (delaying food spoilage during transport and storage) and inflammable liquids (minimizing fire hazards) [2,3].

Polymeric materials are still the dominating materials for gas-separation membranes [4]. Polymers including ethyl cellulose (EC) [5], polycarbonates (PC) [6], polysulfones (PS) [3], poly(1-trimethylsilyl-1-propyne) (PTMSP) [7], and polyphenyleneoxide (PPO) [4] have been investigated for O_2/N_2 separation. Only few polyolefin membranes such as poly(4-methyl-1-pentene) (TPX) have been reported as good membranes for O_2/N_2 separation, and it has been commercialized by the Mitsui Co. The O_2 flux in that membrane is 0.61 GPU and the O_2/N_2 selectivity is 4.15. Further studies in order to improve TPX performance have reported that asymmetric TPX membranes prepared by a phase inversion process had improved flux with a decrease in selectivity [8]. Vinylpyridine-grafted TPX membranes have shown increased O_2/N_2 selectivity (7.5), with an O_2 flux of 1.19 GPU (permeability of 35.6 Barrer) [9]. Other reports have also shown the possibility of preparing oxygen-enriching membranes based on multilayer low-density polyethylene (LDPE) films. The highest oxygen concentration obtained using LDPE three-layer membranes was 44.8% (permeability of 1 Barrer and O_2/N_2 selectivity of 4.2) and for the monolayer it was 39% (permeability of 8.2 Barrer and O_2/N_2 selectivity of 2.7) [10].

Liquid facilitated-transport membranes based on cobalt have also been studied. These membranes with spectacular permeability and selectivity had many problems, mostly related to inadequate stability of the carriers, volatility of the solvent, degradation, and other problems of the immobilized liquid membrane [11]. Generally, membranes with higher oxygen permeability (35–8000 Barrer) or good O_2/N_2 selectivity (7.5–14.4) are made from polymers with a complex molecular structure of graft/block copolymers or other modified polymers that usually are not easy to synthesize [12]. Those polymers usually undergo fast aging during storage and application, which means fast permeability decrease [13].

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Table 1
Physical properties of syndiotactic polypropylene and its copolymers.

Sample	M_w (kg/mol)	M_w/M_n	C.C.		Tacticity (rr%)	Density (g/cm^3)	FFV	T_g (°C)	T_m (°C)	X_c
			(mol%)	(wt%)						
sPP	300	1.8	–	–	88.3	0.8752	0.168	3	119–129	0.19
CsP-H1	270	1.6	1.3	2.6	86.9	0.8740	0.169	1	116	0.13
CsP-H2	240	1.7	2.6	5.1	88.2	0.8733	0.170	1	104	0.11
CsP-H3	240	1.9	8.0	14.8	75.4	0.8588	0.184	−3	no	no
CsP-H4	250	1.7	14.1	24.7	66.7	0.8505	0.192	−8	no	no
CsP-O1	250	1.6	0.3	1.8	87.9	0.8741	0.169	−2	116	0.14
CsP-O2	240	1.6	1.6	8.9	86.8	0.8738	0.170	−6	100	0.11
CsP-O3	250	1.6	3.1	16.1	84.2	0.8671	0.176	−14	93	0.04
CsP-O4	230	1.6	6.9	30.8	79.4	0.8594	0.183	−26	no	no
CsP-O5	260	1.7	10.5	41.3	72.1	0.8497	0.193	nd	no	no

M_w: weight-average molecular weight, M_w/M_n: polydispersity, C.C.: comonomer content, T_g: glass transition temperature, T_m: melting temperature, X_c: crystallinity fraction. nd: not determined, no: not observed.

Among the polyolefins, isotactic polypropylene (iPP) is widely used in the production of food containers and food packing as a gas barrier film (O_2 permeability from 1.1 to 2.5 Barrer) and many patents and research articles are focused on the study of its behavior on biaxially oriented polypropylene film or nanocomposites made from it. In each of these cases the oxygen permeability need to be decreased [14–17]. In general, polyolefins have established themselves as the ideal material for packaging and other disposables, and they are also finding more applications in automotive, appliances, agriculture, electronic construction, communication, etc. [18].

The synthesis of novel polymers with well-defined structures as "tailored" membrane materials is an important trend to improve polymer membranes [19,20]. In this context, the development of catalytic systems and polymerization processes have allowed the production of syndiotactic polypropylene (sPP) with better and controlled microstructure compared to polypropylene synthesized with traditional catalysts [21]. sPP possesses lower crystallinity than iPP, which is an advantage for membrane materials. The crystallinity decreases further with copolymerization, and thus completely amorphous polymers can be synthesized. These polymers with specific properties are interesting materials and perhaps they can find new applications as membrane materials for gas separation.

The objective of this work is to study how comonomer length and content affect the performance of syndiotactic poly(propylene-α-olefin) copolymer membranes. Oxygen permeability and O_2/N_2 selectivity are studied, and they are correlated with crystallinity, glass transition temperature and fractional free volume. Composite membranes prepared on a polyacrilonitrile microporous support, which showed good performance, are also studied.

2. Experimental part

2.1. Materials

The metallocene catalyst ($Ph_2C(Cp)(9\text{-}Flu)ZrCl_2$) from Boulder Scientific and the cocatalyst (methylaluminoxane, MAO) from Aldrich (10% w/v in toluene) were used as received. Toluene was distilled over sodium under an inert atmosphere, and the propylene was purified by passing it through columns containing BASF catalysts R3-11G and R3-12, and a 4 Å molecular sieve. The liquid 1-hexene and 1-octadecene comonomers were purchased from Aldrich and were dried under inert gas prior to use.

Polyacrylonitrile (PAN) microporous membranes manufactured by GKSS (Germany) were used as support; the PAN membrane had the following characteristics: water flux 140 l/m^2 h at 1 bar, average pore diameter of about 20 nm, and average thickness of 40 μm. The cyclohexane used for polymer solution preparation was from Aldrich, and was used as received.

2.2. Polymer synthesis and characterization

All manipulations for synthesis were performed in an inert atmosphere in a dry box or using standard Schlenk line techniques. Syndiotactic polypropylene (sPP) and copolymers with 1-hexene and 1-octadecene (CsP-H and CsP-O, respectively) were synthesized in a 1 L Büchi glass reactor. The main polymer properties are shown in Table 1.

Weight-average molecular weights and polydispersity were determined by gel permeation chromatography (GPC) using a Waters Alliance GPC2000 instrument. Tacticity and comonomer content were determined by ^{13}C nuclear magnetic resonance spectra (^{13}C NMR) recorded on a Varian Inova 300 instrument operating at 75 MHz. Thermal properties were obtained by differential scanning calorimeter (DSC) in a N_2 atmosphere to minimize thermal degradation (Modulated TA Instruments DSC 2920). The crystallinity fraction (X_c) has been estimated using a value of 196.6 J/g (enthalpy of fusion) for a perfect crystallite of sPP [22].

Polymer density (film) was measured according to ASTM D 792. The pycnometric density is based on the difference of between the sample's weight in air and in a nonsolvent (methanol in our case) of known density. The measurement uncertainty was around ±0.003 g/cm^3. The density data were used to evaluate the fractional free volume (FFV), which was calculated using the following relation [23,24]:

$$\mathrm{FFV} = \frac{(V - 1.3V_w)}{V} \tag{1}$$

where $V = 1/\rho$ is the polymer's specific volume, ρ is the polymer's density, and V_w is the estimated van der Waals volume calculated by the group contribution method of Bondi [25].

2.3. Membrane preparation

Dense membranes were prepared by melting the polymer in a HP hydraulic press between two hot plates at a temperature 30 °C higher than its melting temperature (for copolymers with high comonomer content a temperature of 100 °C was enough). In order to prepare films without entrapped air bubbles, the load was gradually increased up to 50 bar over a period of 3 min and then maintained at this load for 3 min. The compression-molded film was then cooled to 40 °C in the compression press through the cooling system of the press plates. The thicknesses of the membranes were measured with a digital micrometer (Deltascope MP2C), and they were between 80 and 180 μm. The values used are from at least 30 single measurements within the whole membrane area.