

Gas permselectivity of carbonized polypyrrolone membrane

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Gas permeability and permselectivity through a polypyrrolone membrane is increased by heat treatment; the selectivity of the membrane carbonized at 700 °C was one or two orders of magnitude higher than that of presently available polymers.

The development of membrane processes for the separation of gas mixtures has made remarkable progress during the last two decades and strong interest exists in the synthesis of membranes that exhibit both higher gas permeabilities and selectivities than presently available polymers.¹ The objective of recent works is therefore to create, in effect, a 'molecular sieve membrane'. Although carbon molecular sieves produced from the pyrolysis of polymeric materials have been studied extensively in adsorption applications, membrane application of carbon molecular sieves does not satisfactorily exhibit a 'molecular sieve effect' because the measured gas selectivities are very low, sometimes lower than those of the original polymer membranes, due to the presence of cracks or large pores causing gas leaks.^{2,3} Here, we report gas permeability and permselectivity through a carbonized polypyrrolone membrane. Recently there have been several reports⁴⁻⁷ that carbon molecular sieve membranes produced from polyimide precursors have higher separation performance than those of conventional polymer membranes. Polypyrrolone is a step-ladder polymer with high thermal and chemical stability. Because of the rigidity of the main chain of polypyrrolone, intersegmental packing and segmental mobility should be inhibited, providing a precursor for a carbon membrane with higher gas permeability and permselectivity than polyimides.

Polypyrrolone was prepared by a two step synthesis (Scheme 1) as described previously.⁸ First, poly(amidoamic acid) **1** was prepared from 3,3',4,4'-diphenylhexafluoroisopropylidene tetracarboxylic dianhydride (6FDA) and 3,3'-diaminobenzidine (DABZ) in *N,N*-dimethylacetamide (DMAC) under nitrogen atmosphere at 0 °C. This prepolymer was cast from DMAC solution at a polymer concentration of 10wt% onto a glass plate. The orange-coloured film was taken off and thermally imidized at 150 °C for 12 h *in vacuo* to give the poly(amino imide) **2**. The intermediate poly(amino imide) was subjected to thermal cyclodehydration at 300 °C for 2 h or at 400 °C for 10 h *in vacuo* to give the polypyrrolone **3**. Polypyrrolone prepared in this way was insoluble and characterized by FTIR spectroscopy and elemental analysis.

Polypyrrolone membranes were heated up to 800 °C at a heating rate of 5–8 °C min⁻¹ under nitrogen atmosphere to give carbon membranes which were *ca.* 40–50 μm in thickness. Under nitrogen atmosphere, polypyrrolone exhibited excellent stability up to 500 °C, without weight loss from the membrane. Thermogravimetry was carried out in flowing He at a heating rate of 5 °C min⁻¹ up to 1000 °C and the evolved gases were simultaneously determined by mass spectroscopy. The gaseous products evolved include carbon monoxide, carbon dioxide, hydrogen fluoride and carbon tetrafluoride, with traces of ammonia and hydrogen cyanide. The total weight loss up to 800 °C was *ca.* 40%. The membrane rapidly degraded at about 650 °C when heated in air.

Permeability coefficients were measured by the vacuum time-lag method at 35 °C and 1 atm. Two different membranes

prepared at each temperature were evaluated. For each membrane, measurements were made three times. The precision in permeability was estimated to be within ±10%. Table 1 shows typical examples of the gas permeability and permselectivity of carbonized polypyrrolone **3** together with the corresponding polyimide **2** and polypyrrolone precursors and the membranes from polyimide precursors.⁴⁻⁷ The gas permeability and permselectivity of polypyrrolone were larger than those of corresponding polyimide. Introduction of a ladder structure in the backbone chains of polyimide enhanced the gas permeability and maintained the permselectivity of gases, due to simultaneous inhibition of chain packing and intramolecular motion.⁸ Furthermore, the permeability of polypyrrolone membranes carbonized at 500–700 °C was enhanced by two orders magnitude compared with the polypyrrolone precursor. The permeability decreased in proportion to the increasing kinetic molecular diameter of the penetrant gas and the permselectivity of the membranes was much higher than those reported in conventional polymeric materials,¹ indicating that the membrane behaves more like a 'molecular sieves'. On the other hand, raising the carbonizing temperature to 800 °C brought about a decrease of permeability and permselectivity. Heating time also affected the membrane performance. Increasing the heating time to 2 h brought about a slight increase of permeability and a sharp decrease of permselectivity. Thus,

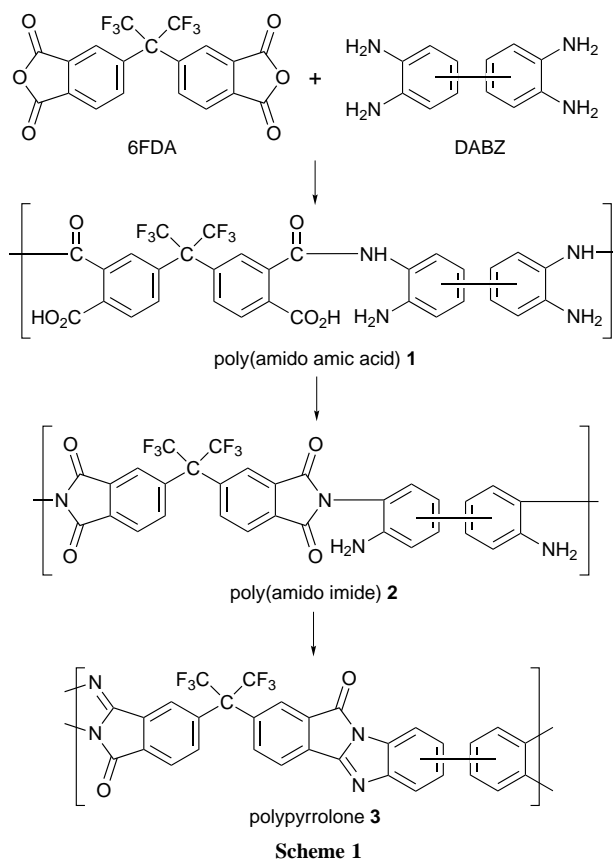


Table 1 Permeability and permselectivity of poly(amino imide) **2** and polypyrrolone **3** at 35 °C

Polymer	Heating conditions	Permeability/ $10^{-10} \text{ cm}^3 \text{ (STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$					Permselectivity				
		H ₂	CO ₂	O ₂	N ₂	CH ₄	H ₂ /CH ₄	CO ₂ /CH ₄	CO ₂ /N ₂	O ₂ /N ₂	
2	150 °C, 12 h	14.6	3.48	1.04	0.171	0.0712	210	49	20	6.1	
3	300 °C, 2 h	87.4	33.0	6.92	1.11	0.507	170	65	30	6.2	
	400 °C, 10 h	176	73.5	19.2	3.15	1.81	97	41	23	6.1	
	500 °C, 1 h	6580	2970	674	74.3	24.7	270	120	40	9.1	
	500 °C, 2 h	6410	3520	815	100	41.1	160	86	35	8.2	
	550 °C, 2 h	5860	2660	669	88.3	51.3	110	52	30	7.6	
	700 °C, 1 h	1720	250	68.1	6.43	1.43	1200	180	39	11	
	500 °C, 1 h	1340	125	35.8	2.18	1.50	890	83	57	16	
	→ 700 °C, 1 h										
	700 °C, 5 h	2180	712	145	16.8	8.44	260	84	42	8.6	
	800 °C, 1 h	25.4	0.178	0.183	0.0235	0.0251	1000	7.1	7.6	7.8	
Kapton ^a	800 °C	—	13	1.2	0.26	—	—	—	50	4.6	
6FDA/BPDA-polyimide ^b	500 °C, 2 h	—	—	20–50 ^c	—	—	—	—	—	8.5–11.5	
	550 °C, 2 h	—	—	15–40 ^c	—	—	—	—	—	11–14	
Kapton ^d	600 °C, 2 h	1500	1200	300	100	—	—	—	12	3	
	800 °C, 2 h	790	200	60	10	—	—	—	20	6	
BPDA-ODA-polyimide ^e	600 °C	—	330	—	11	4.1	—	80	30	—	
	700 °C	—	160	—	2.9	2.7	—	60	55	—	
	800 °C	—	7.8	—	0.26	0.078	—	100	30	—	

^a Measured at 20 °C (ref. 4). ^b Measured by mixed gas at ambient temperature (ref. 5). ^c Permeance [$10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$]. ^d Measured at 100 °C (ref. 6). ^e Measured at 25–30 °C (ref. 7).

polypyrrolone carbonized at 700 °C for 1 h showed the highest membrane performance compared with the carbonized polyimides.^{4–7} This is a promising membrane for gas separation because of its high permeability and permselectivity.

Footnote

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