Application of Poly(phthalazinone ether sulfone ketone)s to Gas Membrane Separation

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ABSTRACT: A series of poly(phthalazinone ether sulfone ketone) (PPESK) copolymers containing different component ratios of bis(4-fluorodiphenyl) ketone and bis(4-chlorodiphenyl)sulfone with respect to a certain amount of 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one were synthesized by polycondensation. Glass transition temperatures of these polymers were adjusted from 263°C to 305°C by changing the ratios of reactants. Gas permeability and selectivity of the dense membranes of the polymers for three kinds of gases $(CO_2, O_2, and N_2)$ were determined at different temperatures. The result indicated that the membrane of PPESK (S/K = 1/1, mol ratio) had an excellent gas separation property. Permeability of the polymer membranes for CO_2 , O_2 , and N_2 was $P_{CO_2} = 4.121$ barrier, $P_{O_2} = 0.674$ barrier, and $P_{N_2} = 0.0891$ barrier, respectively. Separation factors of $\alpha_{O_2/N}$ and α_{CO_2/N_2} were 7.6 and 46, respectively. New material was made into a composite membrane with silicone rubber for blocking up leaks and defects on the surface of its nonsymmetrical membrane. As a result of the test, permeability of the composite membrane was $J_{O_2} = 7.2 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ S}^{-1} \text{ cm}^{-1} \text{ Hg and } J_{N_2} = 0.99 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ S}^{-1} \text{ cm}^{-1} \text{ Hg}$, whereas the α_{O_2/N_2} was still higher than 7. These showed that PPESKs had a bright prospect as the potential membrane material for high-temperature gas separation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2385-2390, 1999

Key words: poly(phthalazinone ether sulfone ketone)s; gas separation; permeability; selectivity; composite membrane

INTRODUCTION

During the progression of membrane material, it is of great significance to develop thermal stable membranes^{1,2}: generally, the membrane materials that show high thermal stability, have fine physical and chemical stability; and they provide technical reliability for operations on liquids or

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gases at high temperatures. The advantages of the development and application of high-temperature membranes include flux enhancement and heat recovery. For example, hot water is sanitized and SO_2 is removed from hot smelter gas streams. As a consequence, they broaden the applications of membrane separation.

It has been proven by many cases of research results that almost all known commercial polymers are not ideal materials for membrane, and cannot meet the demand for materials possessing both high permeability and high selectivity. By increas-

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ing pressure or temperature, permeability for gases is increased, whereas selectivity is decreased.

This article focused on the preparation, physical properties, and membrane properties of novel soluble poly(phthalazine ether sulfone ketone)s (PPESKs) that possess high glass transition temperatures. They provide technical and theoretical reliabilities for application of gas membrane engineering and references for further improving molecular structures and membrane properties.

EXPERIMENTAL

Materials

4-(4-Hydroxyphenyl)-2,3-phthalazin-1-one was synthesized according to the procedure described by Berard and Hay.³ The monomers bis(4-chlorodiphenyl)sulfone and bis(4-fluorodiphenyl)ketone, solvents N,N'-dimethylacetamide (DMAC), chlorobenzene and N-methyl-pyrrolidone (NMP), and catalyst K₂CO₃ are commercial products. They are used without further purification.

Synthesis of Polymers

The precisely weighed monomers, catalyst, solvent, and dehydrant were charged into a threenecked flask in an N₂ atmosphere. Temperature was raised and maintained while the reactants were being stirred; then the temperature was raised after dehydration was completed; the product was filtered, precipitated, and dried three times after completion of the reaction. White floccule PPESK product was obtained. Details are similar to those discussed in the previous articles.⁴ Chemical structure is described in the previous articles.^{3,5}



where A is (1) —CO—, (2) —SO₂—, and X is (1) —F, (2) —Cl. When X = (1), A = (1), the polymer is poly(phthalazinone ether ketone) (PPEK); X = (2), A = (2), the polymer is poly(phthalazinone

ether sulfone) (PPES); and X = (1) and (2), A = (1) and (2), the polymers are PPESKs.

Analysis of Physical Properties

Density of the polymer was determined at 25°C by the density gradient column method using a mixture of carbon tetrachloride and ethanol, and using a density scale, PZ-A-5, made in the Shanghai Scales Factory. Glass transition temperature was examined using a differential scanning calorimeter (Perkin-Elmer, DSC-7) at a heating rate of 10°C min⁻¹ under nitrogen flow. Mechanical properties of synthesized polymers were measured at 23°C using a Shimadzu AG-2000A tester at a crosshead speed of 50 mm min⁻¹. The sample with a dimension of $0.2 \times 6.0 \times 50$ mm³ was prepared by the solution casting method. At least five samples for each composition were tested, and the average value was reported.

A Shimadzu AG-2000A capillary rheomeler was used to perform the rheological characterization using a 5-mm-long, 1-mm-diameter capillary (L/D = 5) at a temperature of 320°C. Shear rate range studied was within 10–200 s⁻¹. The Rabinowith correction and entrance effects were taken into consideration because of the short capillary used. Samples were charged into the capillary as fast as possible and kept in the molten state for 5 min before testing.

Preparation of Films

The polymer was dissolved into NMP, with a concentration of 10%. Then, the solution was cast on a glass plate in a controlled dust-free environment. Relative humidity during casting was maintained at 35–45%. Freshly cast films were first heated for 24 h at ~ 80°C and then for 24 h at ~ 100°C to speed drying in a drier. Polymer films were carefully removed from the plate. The resultant polymer films generally were ~ 20 μ m in thickness.

Characterization of Polymer Films

Characters of polymer films were determined with a K-315-N-01 low-vacuum gas permeability speed indicator (made by Physical and Chemical Precise Machine Corporation, Japan). At least three samples for each composition were tested, and the average value was reported. Purities of the gases used in this institute are all > 99.5%(from the steel cylinder).

Property/Polymer	PSF^{6}	PES^7	$PPES^4$	PPESK $(1:1)^{a}$	PPEK
T_{σ} (°C)	190	225	305	284	263
$\tilde{\text{Density}}$ (g cm ⁻³)	1.24	1.37	1.33	1.34	1.34
Tensile strength (MPa) at rupture	75	85	77	91	104
Tensile modulus (MPa)	2584	2594	1208	1407	1607
Flexural strenath (MPa)	106	128	135	154	172

Table I Comparison of Physical Properties

^a 1 : 1 = ratio between dichlorodiphenylsulfone and difluorodiphenylketone (S/K).

RESULTS AND DISCUSSION

Comparison of Physical Properties of Polymers

As shown in Table I, comprehensive properties of PPES, PPESK, and PPEK are fine, and PPES possessed the highest level of thermal stability. Glass temperatures of PPES and PPESK are 50–80°C higher than that of traditional poly(ether sulfone) (PES), and 85°–115°C higher than that of traditional polysulfone (PSF). New materials have good solubilities and are easy to process when they were dissolved in chloroform and DMAC, etc., at room temperature.

Free Volumes of PPESKs at Different Ratios of Sulfone and Ketone

Based on Van der Waals' volumes of functional groups,⁸ Van der Waals' free volumes, V_w of the repeated units of new PPES, PPESKs, and PPEK were calculated by the summation method of functional groups. According to the datum calculated herein and the average molecular weight of the repeated units (M) and density (ρ) of the polymer determined, the free volume V_f and free volume fraction (FFV) were calculated and listed in Table II, based on the equations as follows:

$$V_f = M/\rho - 1.3V_w \tag{1}$$

$$FFV = V_f / V \tag{2}$$

$$V = 1/\rho \tag{3}$$

As shown in Table II, when S/K is > 1/3, FFV is decreasing with increasing K; when S/K is < 1/3, FFV is increasing when K increases.

Correlation between Permeability of PPES, PPESKs, and PPEK and Temperature

As shown in Figure 1, within the temperature limit of 25°C to 66°C, the correlations of permeability coefficients of PPES, PPESKs, PPEK, and temperatures all coincide with Arrhenius equation $\ln P = \ln Po - Ep/RT$, the lines of $\ln P$ to $1/T(K^{-1})$ were straight, respectively. It could be concluded that PPES, PPESKs, and PPEK are in a glass state in this temperature limit, and the activation energy of gas permeation cannot be varied with temperature. As the temperature rises, the permeability increases, but selectivity decreases. This is because the dependence of the permeability coefficients of CO_2 and O_2 on temperature is not meaningful and the dependence of

Polymer	$T_g~(^{\circ}\mathrm{C})$	$M \;(\mathrm{g\;mol^{-1}})$	$\rho~({\rm g~cm^{-3}})$	$V_w \;(\mathrm{cm}^3 \; \mathrm{mol}^{-1})$	$V_f ({ m cm}^3~{ m g}^{-1})$	FFV
PSF ⁶	186		1.24			0.156
PPES	230	232.25	1.370	112.40	0.101	0.138
PPESK (3:1)	245	443.45	1.340	232.15	0.0658	0.0882
PPESK (1:1)	284	434.44	1.345	227.20	0.0636	0.0861
PPESK (1:3)	274	425.42	1.347	222.00	0.0640	0.0856
PPESK (1:4)	271	423.62	1.348	220.96	0.0638	0.0859
PPEK	263	416.41	1.350	216.80	0.0639	0.0862

Table II Free Volume of Polymers



Figure 1 Effect of temperature on the permeability coefficients of PPES, PPESK, and PPEK gases.

permeability coefficients of N_2 , on temperature, is remarkable. For gases of the same kind, when the permeability coefficients of PPESKs are high, the apparent activation energy of their permeability is low, or the dependence of permeability coefficient on temperature is low. The dependence of the permeability coefficients of PPESK (3 : 1) and PPESK (1 : 1) on temperature is smaller than that of other polymers. (see Table III)

Effects of Introducing Different Amounts of 4,4'-Difluorodiphenylketone (*K*) on Gas Permeability and Selectivity

From Table IV, when S/K is > 1, and K in the previously described polymers increased, the permeability coefficients of all gases increase, and separation factors $\alpha_{\rm CO_2/N_2}$ and $\alpha_{\rm O_2/N_2}$ increase as well. Otherwise, when S/K is < 1, and K of the polymers decrease, the permeability coefficients decrease, and α_{CO_2/N_2} and α_{O_2/N_2} decrease as well. Permeability and selectivity of the PPESK (1 : 1) membrane are best among the PPESKs.

Table IIIApparent Activation Energy E_p (25°C) of PPESKs at Different Values of K

		$E_p \; (\mathbf{J})^\mathbf{a}$	
Polymer/Property	CO_2	O_2	N_2
PPES	19.9	21.7	44.8
PPESK (3:1)	10.1	16.8	29.8
PPESK $(1:1)$	12.8	16.1	29.4
PPESK (1:3)	13.6	19.3	27.3
PPESK (1:4)	16.6	19.9	29.6
PPEK	13.6	18.9	28.8

^a Values of E_p were determined from the slope of the line based on the following equation: $\ln P = \ln P_o - E_p/RT$.

		P (Barrier) ^a		$lpha_{ m CO_2/N_2}$		$lpha_{ m O_2/N_2}$	
Polymer/Property	CO_2	O_2	N_2	$25^{\circ}\mathrm{C}$	60°C	$25^{\circ}\mathrm{C}$	60°C
PPES	0.92	0.15	0.027	34	11	5.7	2.9
PPESK (3:1)	2.94	0.41	0.074	40	15	5.5	2.9
PPESK (1:1)	4.12	0.67	0.089	46	22	7.6	3.8
PPESK (1:3)	2.06	0.16	0.026	39	21	3.0	2.0
PPESK $(1:4)$	1.77	0.13	0.052	34	21	2.6	1.7
PPEK	0.75	0.11	0.042	18	9.0	2.6	1.6

Table IV Permeability and Selectivity for Gases of PPESKs Containing Different Amounts of K

^a 1 barrier = 10^{-10} cm³ (STP) cm/cm⁻² S⁻¹ · cm⁻¹ Hg.

Solubility and Diffusibility for PPES and PPESK (1:1) for H₂ and O₂

For a nonporous membrane, the permeability (P) of a gas through the membrane is determined by the solubility (S) and diffusivity (D) of gas in the membrane matrix. Solubility coefficients of PPES, PPESK (1 : 1), and PSF are for H₂ or O₂ and are tested with the adsorption apparatus (of solution capacity) under high vacuum made by the Dalian Physicochemical Institute of the Chinese Academy of Science. According to the formula $P = D \cdot S$,⁹ diffusibility coefficients are calculated. Results are shown in Tables V and VI.

Table V shows that, as bis(4-fluorodiphenyl)ketone are added (S/K = 1:1) into the polymer, the diffusibility coefficient and solubility coefficient for H₂ are increased.

Table VI shows that the pemeability of PPESK (1:1) and PSF are the same. However, the solubility of PPESK (1:1) is higher than PSF, and the diffusibility of PPESK (1:1) is lower than PSF. This indicates that, because the free volumes of PPESKs are small, their diffusibility coefficients are small. The existence of the N element in the

Table V Permeability of PPES and PPESK (1:1) for H_2

	Polymers		
Property of Membrane	PPES	PPESK (1:1)	
$P \times 10^{10}$ (barrier) $D \times 10^{8}$ (cm ² s ⁻¹) $S \times 10^{3}$ [cm ³ (STP) cm ⁻³	2.4 2.7	$7.1 \\ 5.4$	
$S \times 10^{-1} [\text{cm}^{-1} (\text{SIP}) \text{ cm}^{-1} \text{Hg}]$	0.87	1.3	

structure of PPESK caused the increase of solubility for O_2 .

Property of Composite Membranes of PPESK (1:1)

The material PPKSK (1:1) was nonsymmetrical. Concentration of the polymer in NMP was 27%. Then, it blocked up the leaks and defects on the surface with silicone rubber and was made into a composite. Permeability of the composite membrane is shown in Table VII.

As shown in Tables III–V, permeability of the composite membrane is much larger than that of the dense one, whereas the α_{O_2/N_2} is still ~ 7 . These show that PPESKs have a bright prospect as the potential membrane material for gas separation at high temperatures.

CONCLUSIONS

A series of PPESKs have excellent comprehensive performances. Within the temperature limit of 25°C to 60°C, the correlations of permeability coefficients of PPESK dense membrane against temperature all

Table V	I Pe	ermeability	of PSF	and	PPESK
(1:1) fo	or 0_2				

	Polymer		
Property of Membrane	PPESK (1:1)	PSF	
$P \times 10^{10}$ (barrier)	0.67	0.67	
$D imes 10^8 ~({ m cm}^2 ~{ m s}^{-1}) \ S imes 10^3 ~[{ m cm}^3 ~({ m STP}) ~{ m cm}^{-3}$	2.7	4.2	
$(\text{polym.}) \text{ cm}^{-1} \text{ Hg}]$	2.4	1.6	

Polymer	$J_{\mathrm{O}_2}{}^{\mathrm{a}}$	${J_{\mathrm{N}_2}}^{\mathrm{a}}$	$lpha_{ m O_2/N_2}$
PPESK (1 : 1)	$7.2 imes10^{-6}$	$0.99 imes10^{-6}$	7.2

Table VII $\;$ Permeability of Composite Membrane of PPESK (1:1) for O_2 and N_2

^a In unit of cm^3 (STP) cm^{-2} S⁻¹ cm^{-1} Hg.

coincide with the Arrhenius equation. Apparent activation energy of gas permeation cannot be varied with temperature. The dependence of the permeability coefficients of PPESK (3:1) and PPESK (1: 1) on temperature is smaller than that of other polymers. Permeability and selectivity of PPESK (1 : 1) are best among the PPESKs. Solubility and diffusibility of PPESK (1:1) for H_2 are all higher than those of PPES. That indicated that the addition of bis(4-fluorodiphenyl)ketone led to an increase of permeability of H₂. The solubility of PPESK (1:1) for O_2 is higher than that of PSF, whereas the diffusibility of PPESK (1:1) is lower than that of PSF. The existence of the N element in the structure of PPESK caused the increase of solubility for O₂. Permeability and separability of PPESK (1 : 1) are best among the PPESKs. $\alpha_{\rm CO_2/N_2}$ is 46, and α_{O_2/N_2} is 7.6. In addition, the α_{O_2/N_2} of the composite membranes of PPESK (1 : 1) is still higher than 7. These show that PPESKs have a bright prospect as potential membrane material for high-temperature gas separation.

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