Novel PMDA-ODA Polyimide/Polystyrene Nanocomposite Membranes for Carbon Dioxide Separation

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ABSTRACT

Using N,N-dimethylacetalamide (DMAc) as the suspension media of polystyrene (PS) and poly[styrene-co-(4-vinyl-pyridin)] (PSVP) nanoparticles, in-situ condensation polymerization of dianhydride and diamine was carried out and homogenous polyamic acid solution containing the nanoparticles were obtained. Novel PMDA-ODA nanocomposite membranes with various contents of nanoparticles were prepared by the casting of polyamic acid solution followed imidization. The distribution of the nanoparticles in the membranes and the morphology of the composite membranes were characterized by TEM. Relative homogenous distributions were observed for the polyimide/PSVP nanocomposite membrane, which can be ascribed to the formation of polyamic acid amine salts between pyridinyl and carboxyl. The gas transport properties of CO_2, N_2, and CH_4 for these nanocomposite membranes were investigated at different temperature. It was found that the membrane containing 20% PSVP nanoparticles show both high gas permeability and high permselectivity.

1. INTRODUCTION

Membrane separation of gases has emerged into an important unit operations technique offering specific advantages over more conventional separation procedures (e.g. cryogenic distillation and adsorption)[1-2]. This technique will also contribute to the growth of new research areas, such as carbon dioxide capture. However, even through there are a large number of potential applications for gas separation with polymer membranes, only relatively few of them have become applied in practice. The potential application of a polymer as a separation membrane depends upon the possible throughput and the purity of product. This means that both the permeability coefficient for the gas that is transported more rapidly and the selectivity should be as large as possible. Therefore, in the past twenty years, the control

of gas permeability and permselectivity of polymer membranes has become a subject of strong research with worldwide participation in both industrial and academic laboratories. To achieve such control, it is necessary for us to have a good understanding of the relationship between the properties of the polymers and their gas transport properties.   However, it has been found that simple structural modifications, which lead to increase in polymer permeability usually, cause loss in permselectivity and vice versa[3-7].   This so-called "trade-off" relationship was well described in the literatures[8-9].   It is thus possible to find polymers that exhibit high selectivity and low permeability and vice versa, in addition to that combine low selectivity with low permeability. There do not appear to be any polymers that show the desired trend to large values for both permeability and selectivity.   Expanding the performance envelope generally defined by this "trade-off" relationship is one goal of current research efforts.

In recent years, the efforts and successes in synthesizing a variety of nanostructured materials have provided a new degree of freedom for the development of advanced materials with enhanced or novel properties.   Nanocomposites represent the current trend in developing novel nanostructured materials.   They can be defined as a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale regime.   Kusakabe and his co-workers[10] reported that the permeability of CO_2 in a polyimide/SiO_2 hybrid nanocomposite membrane is 10 times lager than in the corresponding polyimide.   In this paper, organic/organic nanocomposite membranes from PMDA/ODA polyimide and polystyrene-based nanoparticles were prepared.   The gas separation properties for CO_2/N_2 and CO_2/CH_4 were investigated.

2. EXPERIMENTAL

Materials: Pyromellitic dianhydride (PMDA) and oxydianiline (ODA) were purchased from J&K. Pyromellitic dianhydride was recrystallized in dry acetic anhydride and oxydianiline was recrystallized in methanol prior to use. Styrene and 4-vinyl-pyridine were distilled under reduced pressure before use. All other reagents were analytical degree and used as received.

Synthesis of Polystyrene (PSt) and Poly(styrene-co-4-vinylprydine) (PSVP) Nanoparticles.
Standard micro-emulsion polymerization techniques were used.   Reactions were carried out in a three-neck flask at $70 \pm 0.1°C$ equipped with a condenser, mechanical stirrer, and inlet for nitrogen.   A typical monomer emulsion was formed by combining 80g of water, 2g of SDS, 20g of styrene and 2g of divinylbenzene.   The mixture was stirred vigorously to form a monomer emulsion.   Potassium persulfate (0.172g) and 20g of the monomer emulsion were

fed into the reaction vessel.   Prior to polymerization, the reaction mixture was purged with nitrogen, and a small positive pressure of nitrogen was maintained during the synthesis.   The mixture was then stirred vigorously and heated to 70°C for 20 min.   The remaining 84g of monomer emulsion were added to the flask at a rate of 5g/min.   After the feed was completed, the vessel was stirred at 70°C for 5h.   Partial cross-linked polystyrene produced with this procedure yielded particles of average size 66nm.   Poly(styrene-co-4-vinyl-pyridine) nanoparticles were prepared by the same process using the mixture of 4-vinyl-pyridine(5g) and styrene (15g) as the monomer.

Suspension of Polystyrene-based Nanoparticles in Poly(amic acid) Solution. The solvent and dispersion medium, DMAc, was dried over CaH_2, distilled under vacuum, purged with nitrogen, and used fresh.   The polystyrene-based nanoparticles were mixed with DMAc and homogenized by intensive ultrsonication and agitation, to form a 5% (w/w) stable transparent suspension.   The homogeneous dispersions of polystyrene-based nanoparticles with poly (amic acid) in varying composition were made by addition of ODA and PMDA to the suspension at 5°C and then stirring for 6h at 20°C.

Membrane Preparation. Nonporous planar membrane were prepared by casting the mixture of poly(amic acid) and the nanoparticles in DMAc onto glass plates and dried 24h at 100°C under vacuum.   The composite membranes prepared were then thermally cured under vacuum at 150°C for 60 min, 200°C for 60 min, and 250°C for 4h.   The polyimide (PI) composite membranes thus obtained were removed from the glass plates and dried for another 24h at 100°C under vacuum. All composite membranes were treated according to the same procedure. The thickness of the dry composite membranes used for the permeability and diffusivity measurements varied from 20 to 40μm.

Characterization.   The dimensions and size distribution of the nanoparticles were measured on a Matec Applied Sciences CHDF-1100, which separates particles of different size on the basis of the hydrodynamic effects of particles undergoing Poiseulle flow within a capillary tube.   Transmission electron microscopy (TEM) was carried on a JEOL JEM 1200EX.   X-ray photoelectron spectroscopy (XPS) was also used to extract information about the nanoparticle surface.

Measurements of Gas Separation Properties. Mean permeability coefficients, P, and effective diffusion coefficients, D, were measured at 1 and 10atm for different temperature between 30 and 75°C by the time-lag method. The apparatus and experimental procedure employed have been described previous papers[3-4]. From a single transient gas transport

experiment, both permeability coefficient (P) and diffusion coefficient (D) can be obtained. The permeability is given by equation (1):
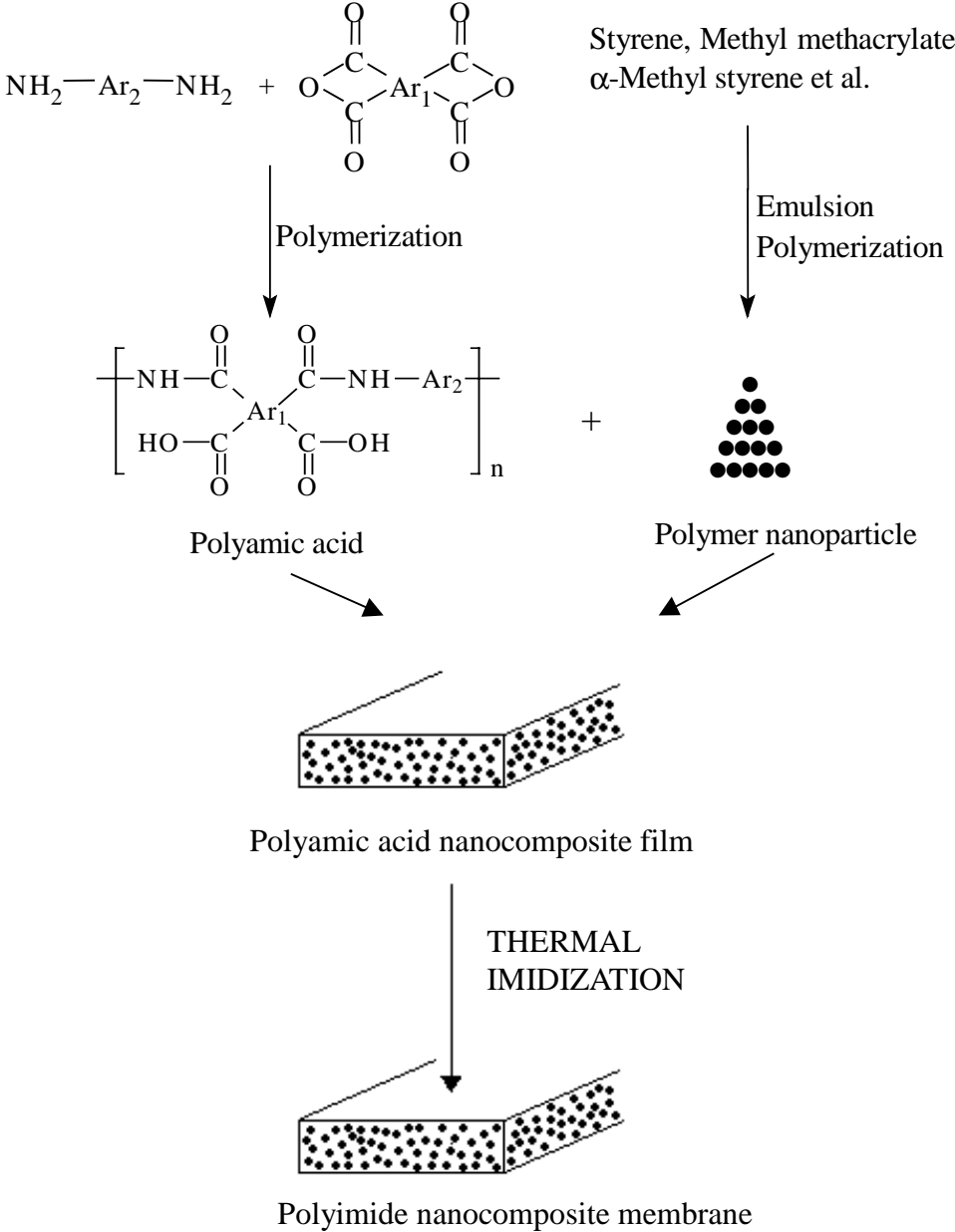
$$P = J_s \cdot \frac{l}{p_2 - p_1} \qquad (1)$$

Figure 1. Schematic representation of membrane preparation process

where l is the thickness of the membrane, J_s is the steady-state rate of gas permeation through a unit area of the membrane, p_2 and p_1 are the upstream and downstream pressures of the gas

component, respectively. Effective diffusion coefficients were calculated from the time-lag θ using equation (2):

$$D = \frac{l^2}{6\theta} \tag{2}$$

The ideal permselectivity of the membranes toward a gas A relative to another gas B were calculated from the individual pure gas permeabilities:

$$\alpha_{A/B} = P_A/P_B \tag{3}$$

where P_A and P_B are the corresponding permeability coefficients of gas A and B, respectively.

3. RESULTS AND DISCUSSION

Preparation and Characterization of the Nanocomposite Membranes

Figure 1 demonstrates the procedure for the preparation of nanocomposite membranes studied in this work. The first stage involves the synthesis of the polystyrene (PSt) and poly(styrene-co-4-vinylpyridine) (PSVP) latex particles in nanometer size. Typical particle size measurements show that every batch produced with the procedure described in experimental yielded particles of average size 63-68nm with peak width at half height of 70-80nm. The size and distribution of the polystyrene-based nanoparticles is influenced by the amount of surfactant, speed of agitation, amount of initial monomer emulsion charge, and amount of persulfate used.

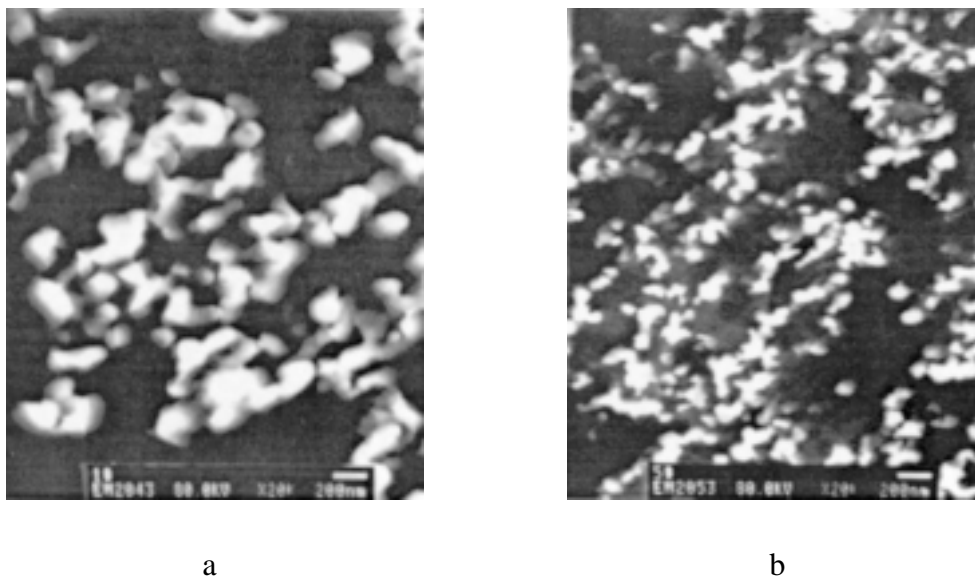a   b

Figure 2. TEM micrographs of PI/PSt (a) and PI/PSVP (b) nanocomposite membranes

The second stage for the preparation of the studied nanocomposite membranes involves

the mixing of the nanoparticles with the polyimide precursor, polyamic acid (PAA), in different fraction.   To achieve a well-dispersed and homogeneous mixture, the nanoparticles were in-situ mixed with PAA solution in DMAc and homogenized by intensive ultra-sonication and agitation.   Stable suspensions were formed and PAA-based nanocomposite membranes were fabricated.   These membranes were thermally cured gradually to prevent the agglomeration of the nanoparticles in the polymer matrix.   TEM micrographs (Figure 2) of the polyimide/polystyrene (PI/PSt) and polyimide/poly(styrene-co-4-vinylpyridine) (PI/PSVP) samples containing 20% nanoparticles reveal that homogeneously dispersed nanocomposite membranes can be prepared with this process.

Pure Gas Separation Properties of the Nanocomposite Membranes

Gas separation properties of these membranes for CO_2, N_2 and CH_4 at 35°C and 10atm are listed in Table 1. It was found that the gas permeabilities for both PI/PSt and PI/PSVP series membranes increase with the increase of nanoparticle fraction from 10% to 20% in the composite membranes.   Meanwhile, with the increase of nanoparticle fraction, the selectivities for CO_2/N_2 and CO_2/CH_4 decreased from 27.4 to 3.19 and from 47.5 to 8.53, respectively, for the PI/PSt nanocomposite membranes.   These results are consistent with the "trade-off" relationship.   However, the PI/PSVP membranes showed us a both increase in permeabilities and selectivities.   As can be seen from Table 1, the selectivities for CO_2/N_2 and CO_2/CH_4 raised from 28.4 to 38.4 and from 35.8 to 41.2 for these membranes respectively. To demonstrate this result, gas diffusion coefficients were analyzed as follows.

Table 1.   Gas permeabilities and permselectivities of membranes at 35°C and 10atm

Membrane	P_{CO2}	P_{N2}	P_{CH4}	$\alpha_{CO2/N2}$	$\alpha_{CO2/CH4}$
PI/10PSt	2.33	0.085	0.049	27.4	47.5
PI/15PSt	2.32	0.090	0.049	25.8	47.3
PI/20PSt	2.90	0.909	0.340	3.19	8.53
PI/10PSVP	3.58	0.126	0.100	28.4	35.8
PI/15PSVP	3.71	0.140	0.102	26.5	36.4
PI/20PSVP	5.65	0.147	0.137	38.4	41.2

P in *Barrers*

It is interesting that the CO_2 diffusion coefficient of PI/PSt membranes increases from 0.302 to 0.503 while that of the PI/PSVP membranes decreases from 0.546 to 0.237 with the nanoparticle fraction raising from 10% to 20%. However, the CO_2 permeability in the PI/PSt membranes is lower than that in the PI/PSVP membranes. The decrease of diffusion coefficient in the PI/PSVP membranes can be described to the relatively homogeneous dispersion of the nanoparticles in polyimide matrix (see Figure 2), and to the compact packing between the polyimide chains and the nanoparticles. These may derive from the partial interaction of pyridinyl group on the surface of the particles with the carboxyl groups of the polyamic acid chains in the membrane fabrication process. The surface pyridinyl groups can be detected from PSVP nanoparticles by XPS spectroscopy. The interaction of tertiary amine with carboxyl group and the formation of amine salts between them were successfully applied for the preparation of polyimide Langmuir-Blodgett films[11]. Therefore, the high CO_2 permeability for PI/PSVP membranes could be reason of the high solubility of CO_2 in the membranes due to the interaction between gas and pyridinyl groups, while the high selectivity may be related to the high diffusion selectivity, especially for membrane PI/20PSVP.

Table 2. Gas diffusivities and diffusion selectivities of membranes at 35°C and 10atm

Membrane	D_{CO_2}	D_{N_2}	D_{CH_4}	D_{CO_2}/D_{N_2}	D_{CO_2}/D_{CH_4}
PI/10PSt	0.302	0.136	0.030	2.22	10.1
PI/15PSt	0.419	0.199	0.057	2.10	7.34
PI/20PSt	0.503	2.94	0.139	0.17	3.62
PI/10PSVP	0.546	0.230	0.060	2.37	9.04
PI/15PSVP	0.517	0.234	0.057	2.21	9.10
PI/20PSVP	0.237	0.175	0.033	1.35	7.14

D in $10^{-8} cm^2/s$

Temperature Dependence of Transport Properties

Within a temperature range in which no significant thermal transitions of the polymer occurs, the temperature dependence of permeabilities and diffusivity can be described by two Arrhenius expressions:

$$P = P_0 \exp(-\frac{E_p}{RT}) \qquad (4)$$

$$D = D_0 \exp(-\frac{E_d}{RT}) \qquad (5)$$

where P_0 and D_0 are pre-exponential factors, E_p is the apparent activation energy for permeation, E_d is the activation energy for diffusion, R is the gas constant, and T is the temperature.
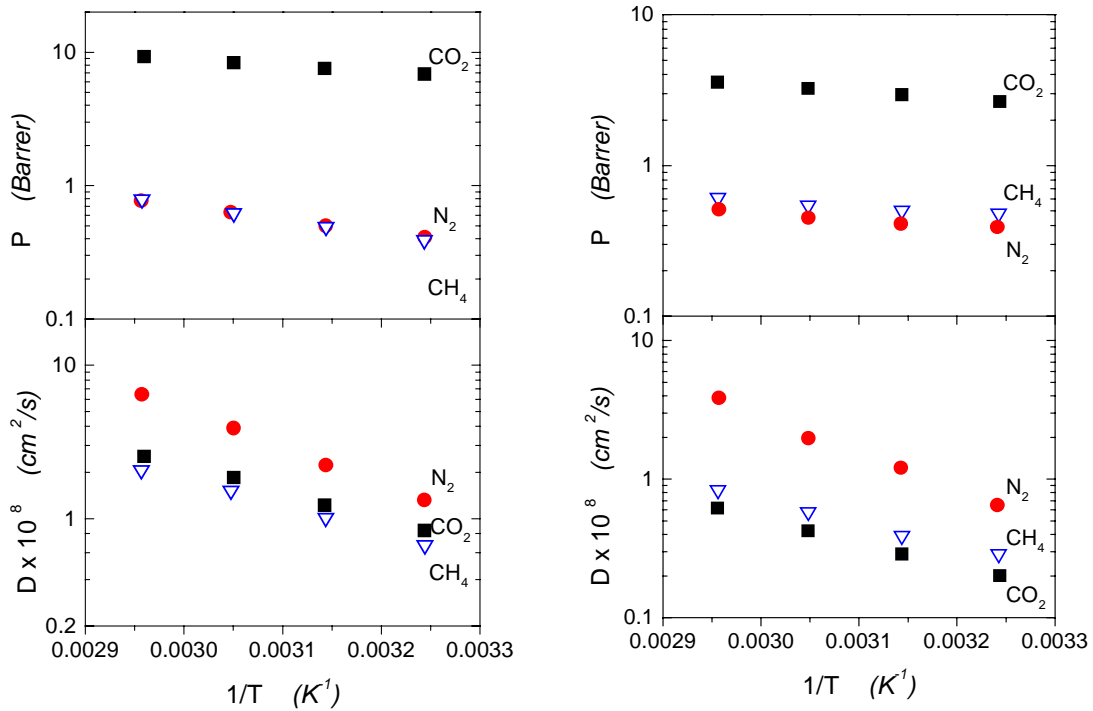

Figure 3. Temperature dependence of the gas permeabilities and diffusivities for PI/20PSt (a) and PI/20PSVP (b) nanocomposite membranes

The effect of temperature on permeabilities and diffusivities for CO_2, N_2, and CH_4 at 1atm upstream pressure for membranes containing 20wt. % of polystyrene and poly(styrene-co-4-vinylpyridine) are presented in Figure 3. From this figure it is clear that the temperature dependence of P and D for the two nanocomposite membranes can be described by the Arrhenius equations (4) and (5).

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