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Gas permeability in polyimides from oxydianiline and isomeric thiaphthalic dianhydride or 1,4-bis(dicarboxyphenoxy) benzene dianhydride

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The gas permeability and permselectivity properties were investigated of polyimides, prepared from 3,3′,4,4′- and 2,2′,3,3′-thiaphthalic dianhydride (*p*-TDPA and *m*-TDPA, respectively), or 1,4-bis(3,4-dicarboxyphenoxy)- and 1,4-bis(2,3-dicarboxyphenoxy) benzene dianhydride (*p*-HQDPA and *m*-HQDPA, respectively), and 4,4-oxydianiline. The polyimides prepared from *meta*-dianhydrides, which have lower chain-segment packing density, possess higher permeability and lower permselectivity than those prepared from *para*-dianhydrides. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyimides; isomeric dianhydrides; gas separation membrane)

Introduction

Aromatic polyimides have attracted much attention as membrane materials for gas separation because of their excellent performance[1]. A substantial amount of work has been devoted to investigating the relationship between the molecular structure of polyimides and their permeability and permselectivity[1–4], indicating that the molecular structure does indeed have a large effect on these properties. Sykes and St Clair found that polyimides prepared from *meta*-diamines, such as *m*-methane dianiline and *m*-diaminobenzophenone, and pyromellitic dianhydride (PMDA) or benzophenone tetracarboxylic dianhydride (BTDA) have lower permeability and higher permselectivity than the corresponding polyimides prepared from *para*-diamine[5]. Stern and colleagues found that the polyimides from *m*-oxydianiline and PMDA or dicarboxyphenyl hexafluoropropane dianhydride (6FDA) have lower permeability and higher permselectivity than the corresponding polyimides from *para*-diamine[6,7]. A similar effect has also been observed for other polyimides prepared from isomeric diamine[8–10]. These results show that *meta*-diamine can improve the permselectivity at the cost of the permeability for these polyimides. Unfortunately, little is known about the effect of isomeric dianhydrides, and it would be desirable to know whether isomeric dianhydrides also affect the permeability and permselectivity of polyimides. Therefore, in this work, we investigated the effect of the isomers of thiaphthalic dianhydride and 1,4-bis(dicarboxyphenoxy) benzene dianhydride on the permeability and permselectivity of the polyimides prepared with 4,4-oxydianiline (ODA).

Experimental

The chemical structures of the dianhydrides used are shown in *Scheme 1*. The poly(thio ether amic acid) precursors were prepared by solution condensation of ODA with a stoichiometric amount of 3,3′,4,4′-thiaphthalic dianhydride (*p*-TDPA) or 2,2′,3,3′-thiaphthalic dianhydride (*m*-TDPA) in dimethylacetamide (DMAc), and the poly(ether amic acid) precursors were prepared by solution condensation of ODA with a stoichiometric amount of 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (*p*-HQDPA) or 1,4-bis(2,3-dicarboxyphenoxy) benzene dianhydride (*m*-HQDPA) in DMAc. The poly(thio ether amic acid) and the poly(ether amic acid) precursors were cast as membranes and then thermally imidized using the same procedure as described previously[11]. Characterization of the polyimides and the permeation experiments were also carried out as described previously[11,12]. The permeability coefficients of the polyimides were measured at an upstream pressure of 10 atm over the temperature range from 30 to 150°C.

Results and discussion

Wide-angle X-ray diffraction (WAXD) curves of all polyimides were broad and structureless, indicating that they all were amorphous. *m*-TDPA–ODA and *m*-HQDPA–ODA have a higher glass transition temperature ($T_g = 288$ and 269°C, respectively) than *p*-TDPA–ODA and *p*-HQDPA–ODA ($T_g = 267$ and 245°C, respectively). Furthermore, *m*-TDPA–ODA and *m*-HQDPA–ODA do not possess a sub-glass transition, but *p*-TDPA–ODA and *p*-HQDPA–ODA have a strong sub-glass transition at 138 and 117°C. This indicates that the chain-segment mobility of *m*-TDPA–ODA and *m*-HQDPA–ODA is much lower than that of *p*-TDPA–ODA and *p*-HQDPA–ODA. It can be expected from molecular structure considerations that the chain-segment packing of *m*-TDPA–ODA and *m*-HQDPA–ODA is lower than that of *p*-TDPA–ODA and *p*-HQDPA–ODA due to changes in molecular conformation and chain-segment movement.

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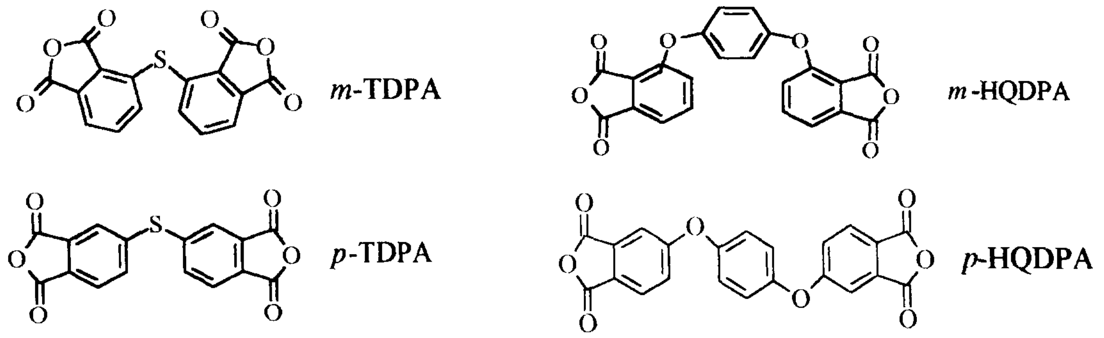

Scheme 1 Structure of isomeric dianhydrides

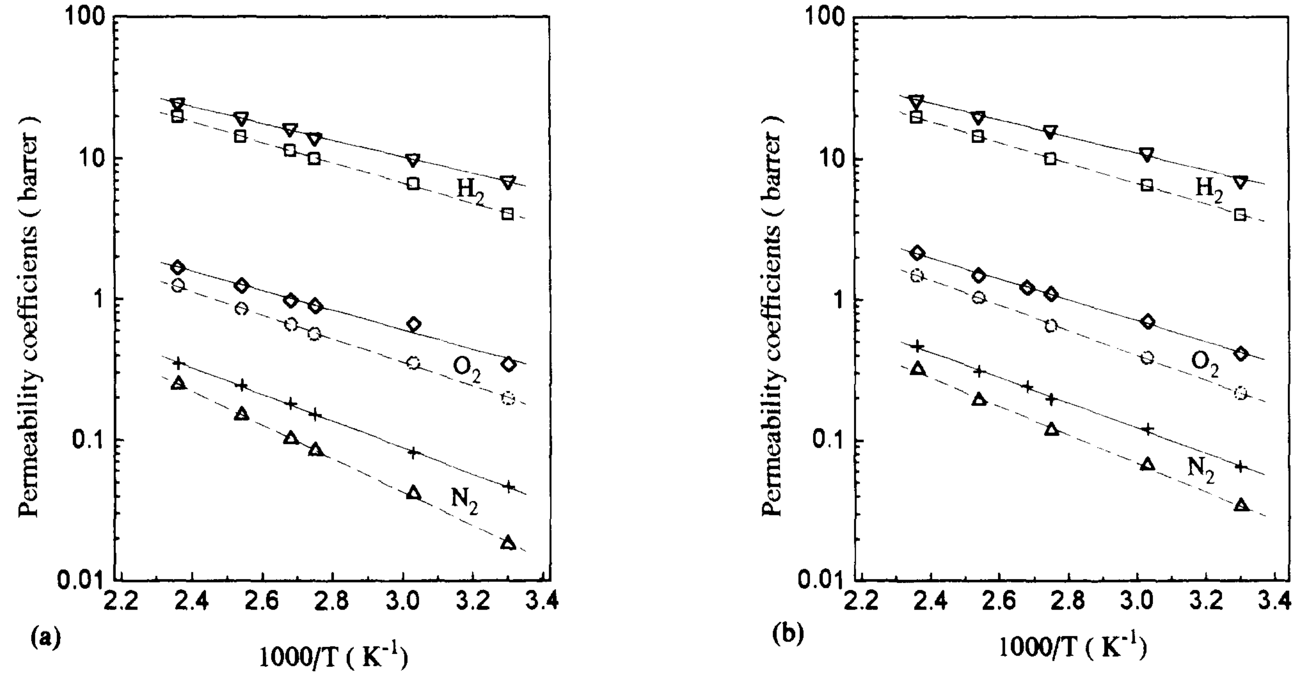

Figure 1 Temperature dependence of permeability for the polyimides. (a) —, *m*-TDPA–ODA; - - -, *p*-TDPA–ODA. Apparent activation energy (kJ mol^{-1}) for *m*-TDPA–ODA: H_2, 11.3; O_2, 14.1; and N_2, 18.0; for *p*-TDPA–ODA: H_2, 13.9; O_2, 16.3; and N_2, 21.9. (b) —, *m*-HQDPA–ODA; - - -, *p*-HQDPA–ODA. Apparent activation energy (kJ mol^{-1}) for *m*-HQPDA–ODA: H_2, 11.7; O_2, 14.5; and N_2, 17.6; for *p*-HQDPA–ODA: H_2, 14.2; O_2, 17.2; and N_2, 20.8

Indeed, the density of *m*-TDPA–ODA and *p*-TDPA–ODA is 1.378 and 1.383 g cm^{-3}, respectively, while that of *m*-TDPA–ODA and *p*-TDPA–ODA is 1.356 and 1.370 g cm^{-3}, respectively.

The permeability coefficients of the four polyimides to H_2, O_2 and N_2 are illustrated in the form of Arrhenius plots in *Figure 1*. All the measurements were carried out in the temperature range from 30 to 150°C. The logarithms of the permeability coefficient of two types of polyimide studies here increase almost linearly with the decrease of the reciprocal of the absolute temperature. The reason is that the polyimides studied are glassy polymers, and the apparent activation energies for gas permeation are unchanged. The apparent activation energies (E_p) of the polyimides for H_2, O_2, and N_2 permeation, which are calculated from the slope of the plots in *Figure 1*, are listed in the figure caption. The permselectivity coefficients of the polyimides for H_2/N_2 and O_2/N_2 at 30 and 100°C and 10 atm are summarized in *Table 1*. The apparent activation energies of the polyimides prepared from *meta*-dianhydrides are lower than those of the corresponding polyimides from *para*-dianhydrides. As a result, the effect of isomeric dianhydrides on the permselectivity at ambient temperature is larger than that at high temperature.

Polymers with low chain-segment packing density have high permeability. Hence, at each temperature, the permeability coefficients of *m*-TDPA–ODA and *m*-HQDPA–ODA to the three gases are larger than those of *p*-TDPA–ODA and *p*-HQDPA–ODA, respectively. Furthermore, the relative increase of the permeability coefficients due to the dianhydride variation is larger for gases of larger molecular volume than for gases of small molecular volume. In other words, replacing *para*-dianhydrides with *meta*-dianhydrides is more effective in increasing the permeability coefficients for gases of larger molecular volume than for gases of small volume. Consequently, the permselectivity coefficients of *p*-TDPA–ODA and *p*-HQDPA–ODA for the gas pairs H_2/N_2 and O_2/N_2 are larger than those of *m*-TDPA–ODA and *m*-HQDPA–ODA, respectively. These facts indicate that the effect of dianhydride isomers on the

Table 1 Permselectivity coefficients of the polyimides

	P_{H_2}/P_{N_2}		P_{O_2}/P_{N_2}	
Polyimide	30°C	100°C	30°C	100°C
p-TDPA-ODA	221	111	10.1	6.3
m-TDPA-ODA	149	89.6	7.5	5.5
p-HQDPA-ODA	118	73.0	6.4	5.0
m-HQDPA-ODA	108	69.4	6.3	5.1

permeability and permselectivity is opposite to that of diamine isomers. The polyimides from *meta*-diamines have lower permeability and higher permselectivity than those from *para*-diamines[6-10]. The main reason is that polyimides from *meta*-diamines have higher chain-segment packing density and lower chain-segment mobility than those from *para*-diamines.

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