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# The copolymer of polypyrrolone and polyphenylquinoxaline for gas separation

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The gas transport properties for $H_2$, $O_2$ and $N_2$ in five random copolymers of polypyrrolone and polyphenylquinoxaline and the two homopolymers have been determined at 30°C and 1 atm. The polypyrrolone exhibits higher selectivity with lower permeability, whereas polyphenylquinoxaline shows lower selectivity with higher permeability. The permeability of the copolymers increase with increasing polyphenylquinoxaline content but the selectivities decrease. Temperature dependence of the gas permeability is reported for one copolymer, which is the same as in other glassy polymers.

**(Keywords: polypyrrolone; polyphenylquinoxaline; copolymer)**

## INTRODUCTION

The separation ability of membranes used in gas separation processes is governed by the transport characteristics of the polymer. A selection of membrane materials is crucial since the ultimate performance of the membrane separation system will be controlled by the inherent capabilities of the materials chosen. Extensive investigations have been made to correlate the chemical structures of polymers with their permeation properties[1–5]. However, only a few studies have been published in the open literature regarding investigations of the gas permeability of copolymers with varying component ratios.

It has been general practice to use more than two components in designing polymeric materials for gas separation[6–9]. Copolymers offer the possibility of preparing membranes with gas permeabilities and selectivities not obtainable with homopolymers.

Both polypyrrolone and polyphenylquinoxaline are thermally stable polymers with high chemical resistance. This paper presents the permeabilities at 30°C to pure $H_2$, $O_2$ and $N_2$ at 1 atm of five copolymers differing in the component ratio of the two polymers. The effect of temperature on the permeability of one copolymer is also addressed.

## EXPERIMENTAL

### *Materials*

*Polypyrrolone and polyphenylquinoxaline.* The monomers and polymers used in this study are shown in *Figures 1* and *2*, respectively. Polypyrrolone was prepared by reacting diphenyl ether dianhydride (DPEDA) dissolved in *N*, *N*-dimethylacetamide (DMAc) with an equimolar amount of tetraaminodiphenyl ether (TADPE) dissolved in DMAc. Polyphenylquinoxaline was synthesized by reacting TADPE and 1,4-bis(phenylglyoxalyl)-benzene (BPGB) in cresol. The solid content of the solution totalled 10% by weight of the mixture.

*Polypyrrolone–polyphenylquinoxaline copolymers.* The preparations of five random copolymers, whose compositions are shown in *Table 1*, were carried out by solution condensation at ambient temperature and at a concentration of 10% solids by weight in an approximate solvent (copolymers A–D in DMAc, E in cresol). Copolymers A–E differ in the relative amounts of DPEDA and BPGB.

### *Film preparation*

Films were prepared by casting the precursor solutions onto clean glass plates and heating at 60°C for 1 h to evaporate most of the solvent. Then the glass plates were moved into an oven and kept at 100°C, 200°C and 300°C each for 1 h under a slow flow of argon. After cooling, the films were stripped from the glass plates by submersion in water. The thicknesses of the films were about 25 μm.

### *Apparatus and gases*

All the gas permeability properties were measured using an RSK Rikaseiki Kogyo K-315N-01 GTR measurement apparatus. The gases were represented as having a minimum purity of 99.5% and were used without further purification.

### *Density and fractional free volume*

The densities of the polymers are shown in *Table 2*. The densities of BPGB–TADPE and the copolymers were measured at 25°C in aqueous calcium nitrate. The density of DPEDA–TADPE was measured at 25°C in a mixture of methylene chloride and chloroform. The densities of the solutions were determined using a PAAR DMA45 density meter.

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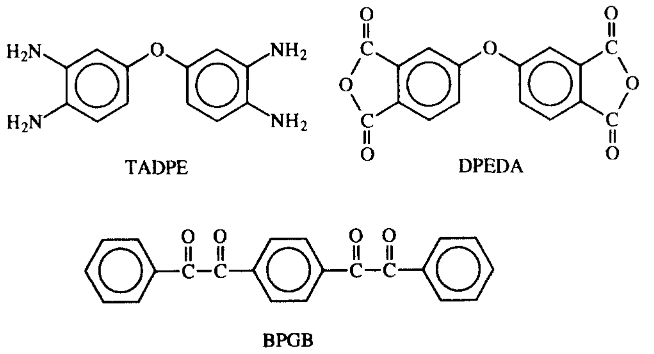

**Figure 1** Monomers used in this study

The fractional free volume (*FFV*) was estimated by the method of Lee[10], which uses the group contribution correlation of Van Krevelen[11] for calculation of the van der Waals volumes. The *FFV* is dependent upon the occupied volumes assigned to the constituent moieties making up the polymer.

## RESULTS AND DISCUSSION

The permeabilities and selectivities of the polymers to the pure gases $H_2$, $O_2$ and $N_2$ at 30°C and 1 atm are listed in *Table 3*. The values of $P$ for the gases in the polymers studied decrease in the order $P_{H_2} > P_{O_2} > P_{N_2}$, which is also the order of increasing kinetic molecular diameter of these penetrants.

**Table 1** Compositions of the copolymers

| Copolymer | BPGB (mol%) | DPEDA (mol%) | TADPE (mol%) |
|---|---|---|---|
| A | 10 | 90 | 100 |
| B | 30 | 70 | 100 |
| C | 50 | 50 | 100 |
| D | 70 | 30 | 100 |
| E | 90 | 10 | 100 |

**Table 2** Physical properties of the polymers

| Polymer | $\lambda_{inh}$ (dlg$^{-1}$) | Density (g ml$^{-1}$) | Fractional free volume |
|---|---|---|---|
| DPEDA–TADPE | 1.12[a] | 1.379 | 0.1465 |
| Copolymer A | 1.19[a] | 1.348 | 0.1580 |
| Copolymer B | 1.24[a] | 1.310 | 0.1646 |
| Copolymer C | 1.27[a] | 1.284 | 0.1659 |
| Copolymer D | 1.38[a] | 1.255 | 0.1702 |
| Copolymer E | 1.64[b] | 1.227 | 0.1748 |
| BPGB–TADPE | 1.89[b] | 1.206 | 0.1822 |

[a] At 30°C, 0.5 g dl$^{-1}$ in DMAc
[b] At 30°C, 0.5 g dl$^{-1}$ in cresol

As shown in *Table 3* BPGB–TADPE is more permeable than DPEDA–TADPE by factors of 1.5, 7.8 and 12.2 for $H_2$, $O_2$ and $N_2$, respectively. Correspondingly, the ideal selectivities for $H_2/N_2$ decrease by factors of 4.2 and 0.49, respectively.

The significantly higher selectivity but lower permeability of DPEDA–TADPE for each gas may be due to

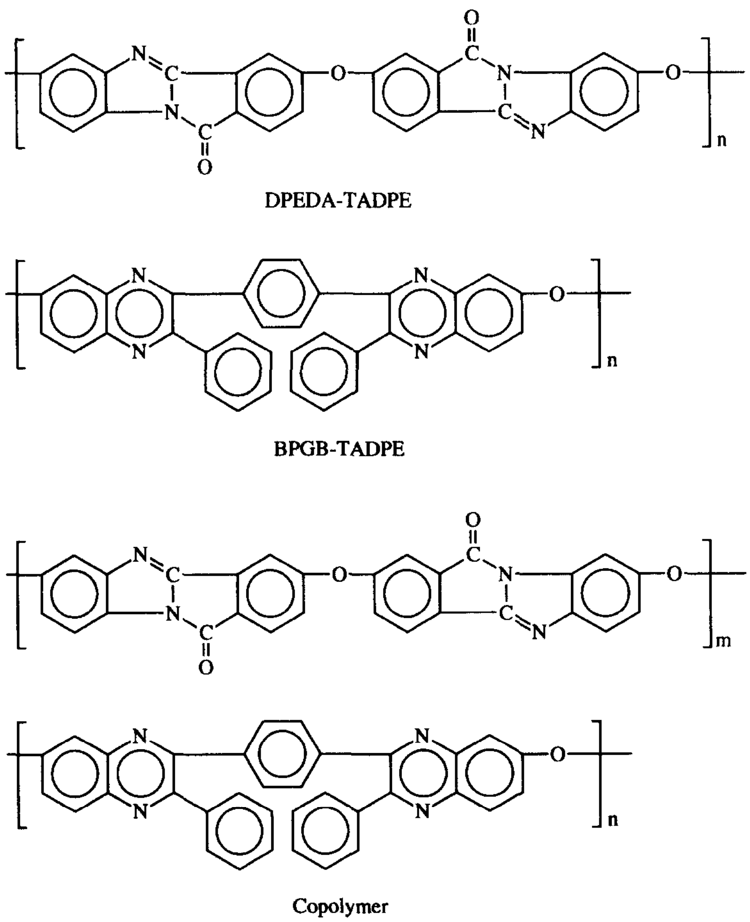

**Figure 2** Polymers used in this study

**Table 3** Permeabilities and selectivities of the polymers at 30°C and 1 atm

| | Permeability (Barrer)[a] | | | Ideal selectivity | |
|---|---|---|---|---|---|
| Polymer | $H_2$ | $O_2$ | $N_2$ | $H_2/N_2$ | $H_2/N_2$ |
| DPEDA–TADPE | 6.88 | 0.223 | 0.261 | 260 | 8.5 |
| Copolymer A | 7.01 | 0.294 | 0.0379 | 185 | 7.8 |
| Copolymer B | 7.95 | 0.423 | 0.0580 | 137 | 7.3 |
| Copolymer C | 11.6 | 0.886 | 0.132 | 88 | 6.7 |
| Copolymer D | 13.2 | 1.24 | 0.202 | 65 | 6.1 |
| Copolymer E | 16.4 | 1.71 | 0.286 | 57 | 6.0 |
| BPGB–TADPE | 17.2 | 1.97 | 0.344 | 50 | 5.7 |

[a] Barrer = $10^{-10}$ cm$^3$ (STP) cm cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$

**Table 4** Temperature dependence of permeabilities and selectivities for copolymer C at 1 atm

| | Temperature (°C) | | | |
|---|---|---|---|---|
| Permeability/selectivity | 30 | 60 | 75 | 90 |
| $P_{H_2}$ (Barrer) | 11.6 | 18.8 | 24.6 | 30.6 |
| $P_{O_2}$ (Barrer) | 0.886 | 1.65 | 2.03 | 2.58 |
| $P_{N_2}$ (Barrer) | 0.132 | 0.282 | 0.407 | 0.544 |
| $\alpha_{H_2/N_2}$ | 88 | 67 | 60 | 56 |
| $\alpha_{O_2/N_2}$ | 6.7 | 5.9 | 5.0 | 4.7 |

the tighter intersegmental packing and lower intrasegmental mobility, for the backbone of the polymer contains units of four condensed rings, a structure which shows extremely high rigidity. Stiffer polymers generally have a higher selectivity because they behave more like 'molecular sieves'[12] and are better able to discriminate between penetrant molecules of different sizes and shapes. Compared with DPEDA–TADPE, BPGB–TADPE possesses a larger *FFV*. Generally, the polymer with the larger *FFV* has the higher permeability. The larger *FFV* of BPGB–TADPE may be attributed to the bulky phenyl side group in the chain. The bulkier phenyl substituents may act as 'spacers', leading to a disruption of chain packing and cause an increase in permeability for all gases, especially for the larger penetrants resulting in a decrease in selectivity.

Referring to *Table 3*, it can be seen that all gas permeabilities of the copolymers increase with increasing BPGB–TADPE content. Paul[13] has suggested that the permeability coefficient $P$ of a copolymer can be estimated from the values $P_i$ of its $i$ constituent homopolymers by means of

$$\ln P = \sum q_i \ln P_i \tag{1}$$

where $q_i$ is the volume fraction of the $i$th constituent homopolymer.

Since BPGB–TADPE is more permeable than DPEDA–TADPE, the permeabilities of the copolymer increase with the BPGB–TADPE content. *Figure 3* shows the relationship between the weight fraction of BPGB–TADPE and the *FFV*, and indicates that the *FFV* increases with increasing BPGB–TADPE content. As mentioned above, the larger the *FFV*, the more permeable a polymer is. Regarding the change in the ideal selectivity of the copolymers, it can be seen that the ideal selectivity decreases with increasing BPGB–TADPE content. In general, there is a trade-off between gas permeability and selectivity. So, the decrease in the selectivity is normal since gas permeability increases with increasing BPGB–TADPE content.

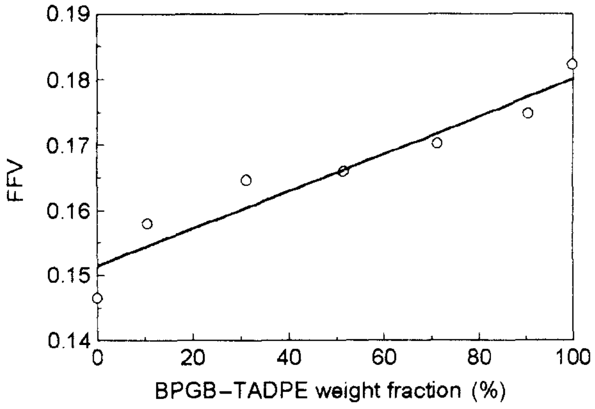

**Figure 3** *FFV* as a function of BPGB–TADPE weight fraction

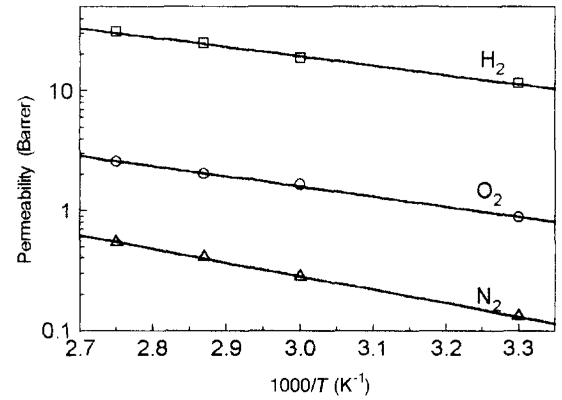

**Figure 4** Arrhenius plots of permeability for various gases in copolymer C at 30–90°C and 1 atm

The permeability and selectivity data for copolymer C for various gases over a temperature range of 30–90°C are listed in *Table 4*. As the temperature is raised from 30°C to 90°C, the permeability increases and the selectivity decreases correspondingly, i.e. $P_{H_2}$, $P_{O_2}$ and $P_{N_2}$ increase by factors of 1.6, 1.9 and 3.5, respectively, while the $H_2/N_2$ and $O_2/N_2$ selectivities decrease by 36% and 30%. The decrease in selectivity with increasing temperature for each gas pair is not surprising, since this is known to occur for most gas separations. Within temperature ranges where no significant polymer phase thermal transitions occur, the effects of temperature on permeability can be described by an Arrhenius expression[1,14,15]

$$P = P_0 \exp(-E_p/RT) \tag{2}$$

where $P_0$ is the pre-exponential factor, $E_p$ is the apparent activation energy for permeation and $R$ is the gas constant.

*Figure 4* shows the permeabilities of the three gases on a logarithmic scale, plotted *versus* inverse temperature according to equation (2). The permeability of copolymer C has the same temperature dependence as the permeability of other glassy polymers[16–18]. The activation energies of permeation $E_p$, obtained as the gradients of the lines in *Figure 4*, are 3.60 kcal mol$^{-1}$, 3.94 kcal mol$^{-1}$ and 5.42 kcal mol$^{-1}$ for $H_2$, $O_2$ and $N_2$, respectively, which follow the expected general trends. In particular, $E_p$ increases as the penetrant size increases.

## CONCLUSIONS

The significantly higher selectivity but lower permeability of DPEDA–TADPE may be due to the tighter chain packing and lower intrasegmental mobility. The bulkier phenyl substituents in BPGB–TADPE may act as 'spacers', leading to a disruption of chain packing, and cause an apparent increase in permeability for all gases and decrease in selectivity. The gas permeabilities of the copolymers increase with increasing BPGB–TADPE content, while the selectivities decrease. In the temperature range 30–90°C, the permeabilities of copolymer C increase and the selectivities decrease correspondingly as the temperature is raised. The effects of temperature on the gas permeabilities of copolymer C can be described by an Arrhenius expression.

## ACKNOWLEDGEMENT

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