

Influences of Van Der Waals Volume of Substitute Groups on CO₂ Permselectivity of Polyimide-A Molecular Simulation Study

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ABSTRACT: Polyimide (PI) as a typical glassy polymer material was investigated by molecular simulation to reveal the relationship between polymer molecular structure and its gas separation properties. The influences of van der waals volume (V_w) on CO₂ permselectivity of PI polymers (with four kinds of backbone substitute groups and a series of side substitute groups from small to large volume) and V_w was proposed as an intermediate to establish the relationship between the substitute group and permselectivity. The results show that the CO₂ permeability (P) simply increases and CO₂/N₂ selectivity (S) decreases with the increasing V_w of side substitute groups. The linear fitline of P - V_w is much suitable to describe and predict the effect of the increasing V_w of side substitute group on improving permeability by analyzing the experimental and calculated CO₂ permeability. The increasing V_w of backbone substitute group can slow down the increasing of CO₂ permeability, but result in the decreasing first and then recovering to the original level. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41082.

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INTRODUCTION

Carbon dioxide (CO₂) is the primary greenhouse gas that causes the global warming, where membrane gas separation technology applied in CO₂ separation is a flourishing industrial important procedure offers a number of benefits over other separation technologies, such as small plants, easy operation, and low costs.¹ The CO₂ separation performance of gas separation technology is largely dependent upon the properties of membrane materials. The ideal performance of a membrane material is expected to exhibit high permeability (P) and selectivity (S), however, as permeability increases while selectivity decreases, permeability and selectivity is a trade-off relationship for most polymer membranes.² Among various polymer materials, polyimide (PI) as one of the typical glassy polymer materials has attracted much attention due to its high selectivity combining with outstanding thermal stability properties.³ Without exception, PI also suffers a trade-off between permeability and selectivity like most glassy polymer materials.^{4,5} Although various side or backbone substitute groups are introduced to PI polymers for improving its permselectivity, the change of thermophysical parameters are also changed in accompany with the CO₂ separation performance.⁶ It is of great importance to reveal the effect of substitute group on improving the CO₂ separation performance and the thermophysical parameters of PI.

In current studies, the thermophysical parameters associated with permeability are mainly focused on glass transition temperature (T_g) and fractional free volume (FFV). Until now, a qualitative relationship between T_g and permeability has been widely accepted, and that is the lower T_g corresponding to the higher permeability for glassy polymer materials.⁷⁻¹⁰ In recent years, a quantitative correlation between FFV and gas diffusion coefficients has been established,¹¹⁻¹⁵ and it reflects that high FFV of glassy polymer materials is preferred to provide more network space for gas transport. It is well known that the substitute group is generally expressed by the structural scheme rather than a quantitative index. Then, both T_g and FFV cannot bridge the direct relationship between the substitute group and permselectivity. A direct quantitative index is necessary to straightly represent the substitute group, for the sake of establishing a quantitative relationship between substitute group and permselectivity.

Van der waals volume (V_w), as an important thermophysical parameter, can fully represent both the contribution of total atoms and the volume of the whole group. Moreover, V_w can be conveniently calculated by the group contribution method of molecular simulation instead of experimental measurement. In recent years, molecular simulation brings together a unique combination of quantum mechanics, statistical mechanics,

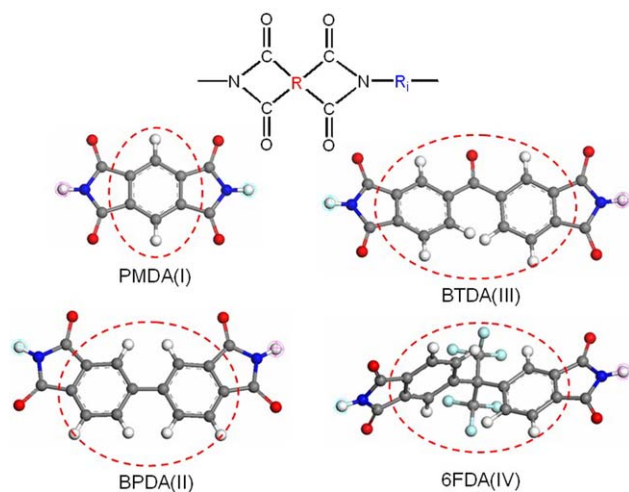


Figure 1. Basic structure of the PI polymer and the backbone substitute group of PMDA(I), BPDA(II), BTDA(III), 6FDA(IV). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

classical molecular dynamics, and multiscale modeling,¹⁶ providing an insight understanding of polymer structure and permselectivity property.¹⁷ By constructing the designed polymer cell, the diffusivity^{18,19} and solubility coefficients²⁰ can be conveniently calculated using molecular dynamic simulation and Grand Canonical Monte Carlo (GCMC) simulation, respectively. However, both of the two simulation methods have high calculation costs as the polymer cell must endure fully state equilibrium for at least several nanoseconds according to the total number of atoms in the system. The synthesis module based on structure-property estimation equation embedded in Material studio software can easily calculate the above thermophysical parameters like V_w , T_g , and FFV by constructing polymer structure while omitting the dynamic equilibrium and relaxation. Above all, V_w is expected to be a bridge between thermophysical parameter and performance property of polymer, playing an intermediate role in establishing the mathematical relationship between the substitute group and permselectivity.

In this work, PI with four kinds of backbone substitute groups and a series of side substitute groups from small to large volume were selected as representative glassy polymer. The objective of our work is to investigate the influence of V_w of side substitute group on the permselectivity of the PI polymers. The V_w of the side substitute group, backbone substitute group and the total PI polymers were calculated by molecular simulation. The linear fitlines of $P-T_g$, P -FFV, $P-V_w$, $S-V_w$, T_g-V_w , and FFV- V_w were established, respectively, to obtain quantitative correlations between the thermophysical parameter and performance property. Moreover, the validity of the linear fitline was verified by the comparison of the predicted CO_2 permeability with the reported experimental data.

POLYMER CONSTRUCTION AND SIMULATION CALCULATION

Polymer Constructions

The basic structure of the PI polymer and the four kinds of backbone substitute groups are shown in Figure 1. The backbone substitute groups include pyromellitic dianhydride (PMDA), biphenyl-

tetracarboxylic acid dianhydride (BPDA), benzophenone-3,3,4,4-tetracarboxylic acid dianhydride (BTDA), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), which are marked as PMDA(I), BPDA(II), BTDA(III), and 6FDA(IV), respectively. First, the volume of the backbone substitute groups follows the increasing order of $I < II < III < IV$. Second, the structure of the backbone substitute groups is changed from plane to stereo structure with the increasing dihedral angles.

The structure of the side substitute group R_i is summarized in Table I. The side substitutes group a , b , e , and f are chosen for the four groups of the PI polymer. In addition, the side substitute group c and d are chosen to form a series of side substitute group for group I and IV. Due to the lack of experimental data, the side substitute group c' and d' are chosen instead of c and d to form a series of side substitute group for group II and III.

Calculation of T_g

Compared with the high calculation cost of molecular dynamic simulation, the calculation of T_g based on the group contribution method is much easy and quick. Besides, the error with about 10% derivation based on the group contribution method by the Synthia module of Material Studio 4.0 is acceptable^{10,18,21} due to the lack of the experimental data of T_g of the selected PI series polymers in this study. T_g can be calculated by eq. (1):

$$T_g = \frac{\sum Y_{gi}}{M_w} \quad (1)$$

The procedure of calculation mainly includes three steps. First, the repeat unit of each polymer segment was defined by setting

Table I. Side Substitute Group of PI

Mark of R_i	Name of R_i	Structure of R_i
a	mTrMPD	
b	ODA	
c	MDA	
c'	DATPA	
d	IPDA	
d'	BAHF	
e	BAPHF	
f	BATPHF	

the head and tail atom. Then, the polymer segments with the defined repeat unit were fully energy minimized and geometry optimized. The contribution Y_{gi} of each group to the “molar glass transition function” Y_g were chosen from literature.²² M_w is the molecular weight of polymer, g/mol.

Calculation of FFV

FFV of each PI polymer can be calculated as follows⁶:

$$\text{FFV} = \frac{V_i - V_0}{V_i} \quad (2)$$

$$V_i = M_w / \rho_i \quad (3)$$

$$V_0 = 1.3 V_w \quad (4)$$

where V_i is the molecular volume of PI polymer, cm^3/mol ; V_0 is the occupied volume of chains, cm^3/mol ; V_w is the van der Waals volume of the whole PI polymer, cm^3/mol . ρ_i is the density of polymer material, g/cm^3 ; i represents the mark of side substitute group.

Calculation of V_w

V_w of each side substitute group R_i , backbone group, or the whole PI polymer is given by eqs. (5–7)²³:

$$V_w = N_A \left[\frac{4}{3} \pi R^3 - \sum \pi h_i^2 \left(R - \frac{h_i}{3} \right) \right] \quad (5)$$

$$h_i = R - \frac{l_i}{2} - \frac{R^2}{2l_i} + \frac{r_i^2}{2l_i} \quad (6)$$

$$\Delta V_{w(m-n)} = V_{w-m} - V_{w-n} \quad (7)$$

V_w is estimated by the group contribution method.²⁴ N_A is the Avogadro's number (6.02×10^{23}). R is the radius of a given atom A , r_i is the radius of atom i covalently bonded to A , and l_i is the bond distance between the atoms A and i . $\Delta V_{w(m-n)}$ represents the volume difference of V_w with different side group from a to f or backbone substitute group from I to IV.

Linear Fitline of Thermophysical Parameter and Performance Property

The experimental permselectivity data of CO_2/N_2 and CO_2/CH_4 for PI polymers were chosen from the reported literatures.^{5,25–31} For each group of the PI polymer, the linear fitline was established according to the relationship of the thermophysical parameter and performance property based on the following equation:

$$L_{i-j} = k_{i-j} \theta_j + b_{i-j} \quad (8)$$

where, L_{i-j} represents the calculated linear fitline. i represents the groups of the PI series polymers from I to IV, j represents permeability (P), selectivity (S), T_g (T), and FFV (F), respectively. k is the slope of linear fitline, b is the intercept, θ represents V_w of each side substitute group.

RESULTS AND DISCUSSION

Effects of Side and Backbone Substitute Groups on V_w of PI Series Polymers

The molecular volume of PI is changed due to the side and backbone group modification, therefore the V_w of each side substitute group R_i , $\Delta V_{w(\text{IV-I})}$, and $\Delta V_{w(\text{III-II})}$ were calculated in terms of eqs. (5–7) as shown in Figure 2. The V_w of side substitute group from a to f exhibits a single increasing trend as

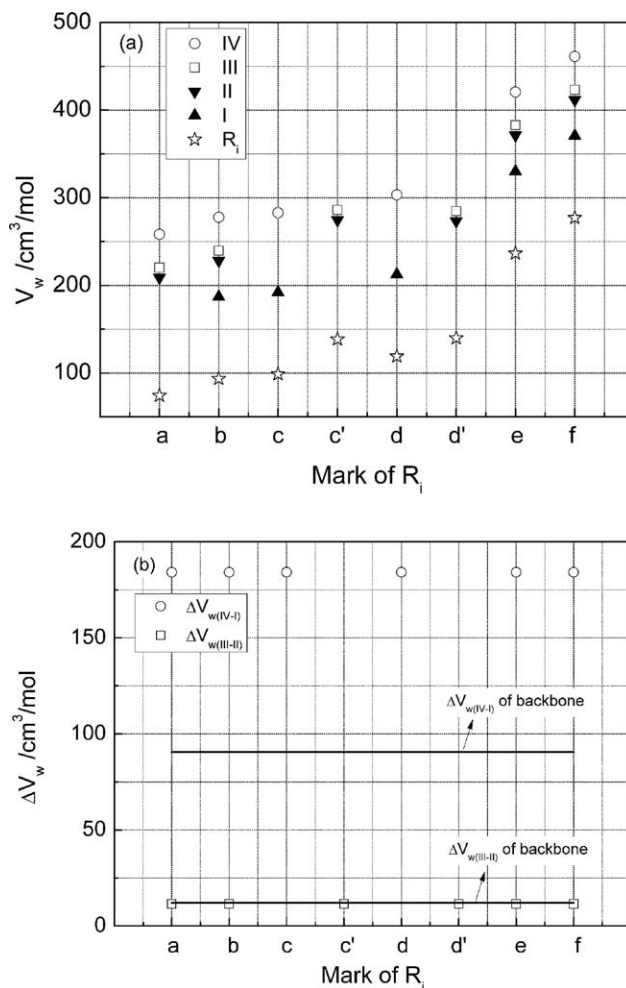


Figure 2. (a) V_w of side substitute group R_i and PI series polymers, (b) difference of V_w between group (IV–I) and (III–II).

shown in Figure 2(a). This increasing trend is owing to the increase of the number of total atoms from 18 (group a) to 42 (group f). For each side substitute group, the V_w of the whole PI polymers increases obviously from group I to IV due to the increasing of backbone substitute group. This is in accordance with the widely accepted rule that the large side substitute group of glassy polymers has the large value of V_w .³² Besides, the ΔV_w of different side substitute groups is independent with the complexity of backbone substitute group. For example, the side substitute group b and c are two connected benzene rings and the $\Delta V_{w(c-b)}$ of $5.1 \text{ cm}^3/\text{mol}$ just equals to the pure volume difference between the ether of group b and the ethyl of group c . By contrast, the side substitute group e and f are four connected benzene rings while the $\Delta V_{w(f-e)}$ is also just the pure volume difference of the two groups.

Figure 2(b) shows the difference of ΔV_w calculated by backbone substitute group and the whole PI polymer from I to IV. It is interesting to find that the values of $\Delta V_{w(\text{IV-I})}$ and $\Delta V_{w(\text{III-II})}$ of the whole PI polymer is stable, which are 184.15 and 11.39 cm^3/mol , respectively. The large difference between $\Delta V_{w(\text{IV-I})}$ and $\Delta V_{w(\text{III-II})}$ can be explained from two aspects. One reason is the configuration change of backbone substitute

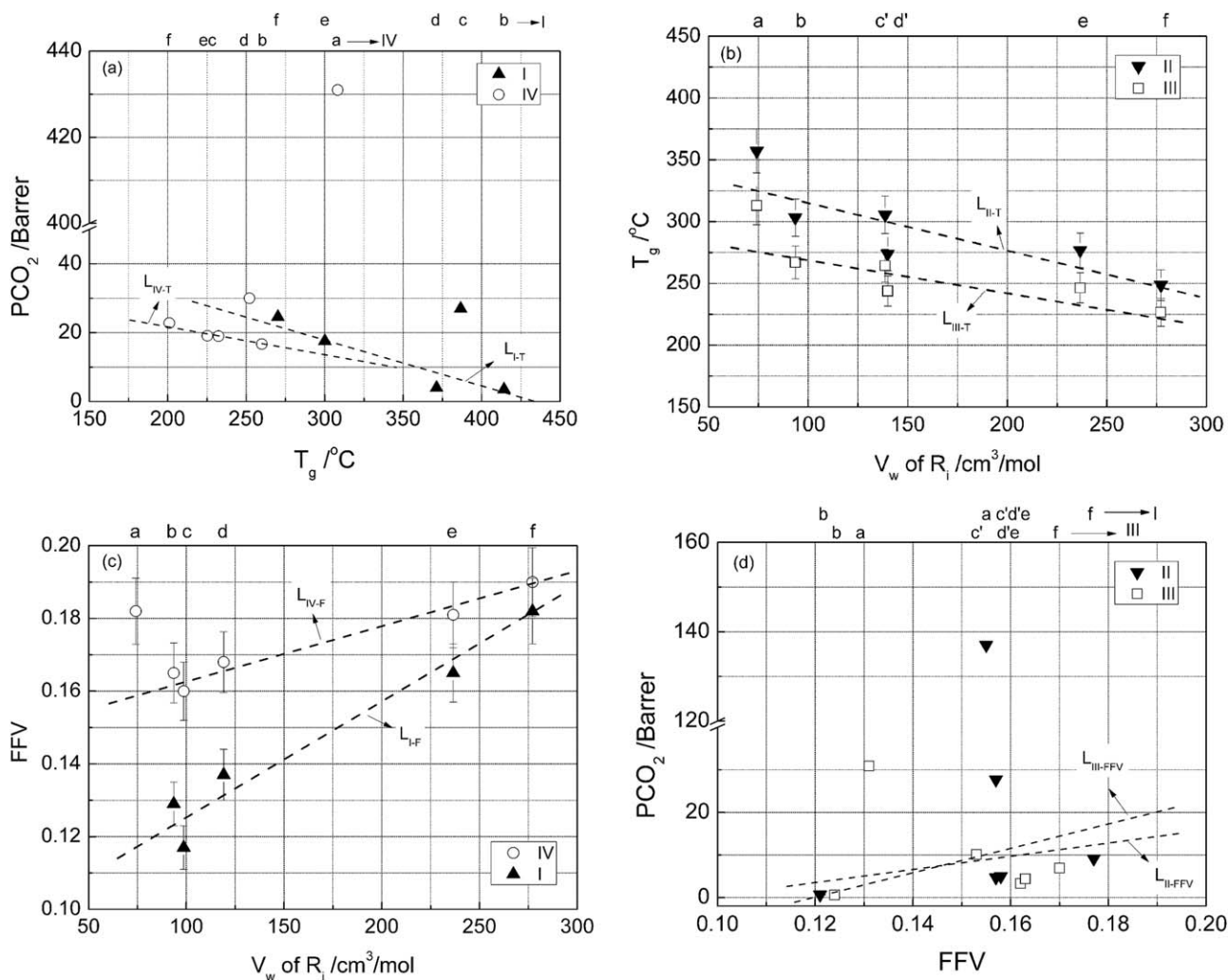


Figure 3. Relationship between (a) P and T_g of group I and IV, (b) P and T_g of group II and III, (c) P and FFV of group I and IV, and (d) P and FFV of group II and III.

group. The flat structure of group I is changed to the stereo structure of group IV with a dihedral angle of 110.2° . It is larger in comparison with the configuration change of only 38.5° from group II to III. The other reason is the difference of the increasing number of total atoms. The number of total atoms is increased from 6 (group I) to 21 (group IV) while that is only increased from 12 (group II) to 14 (group III).

Additionally, it should be noted that the $\Delta V_{w(IV-I)}$ and $\Delta V_{w(III-II)}$ of backbone substitute group is only 90.64 and 12 cm^3/mol , respectively. They are far lower than the $\Delta V_{w(IV-I)}$ and $\Delta V_{w(III-II)}$ of the whole PI polymers. It indicates that ΔV_w is not only determined by the side substitute group but also systematically further enhanced due to the existence of large and stereo backbone group such as group IV. Due to the large configuration change from group I to IV, the $\Delta V_{w(IV-I)}$ of backbone substitute group is easily enhanced from 90.64 cm^3/mol to 184.15 cm^3/mol of the whole PI polymer. The configuration change from group II to III is only 38.5° , therefore the $\Delta V_{w(III-II)}$ between the backbone and whole PI polymer is close, that is 12 and 11.39 cm^3/mol , respectively.

Relationship Between Permeability and T_g or FFV

The quantitative relationship between diffusion coefficient and FFV is already existed, but the direct quantitative relationship between permeability and T_g or FFV are lack in the previous studies. Therefore, the quantitative relationship between P and T_g and P and FFV are separately established in this work, and the results of fitlines are shown in Figure 3.

On one hand, the CO₂ permeability of the four groups of PI polymers simply decrease with the increasing of T_g as shown in Figures 3(a) and (b), which follows the current views that the increasing of T_g can reduce the flexibility and mobility of glassy polymer chain.⁵ Conversely, the CO₂ permeability of the four groups of PI polymers increase with the increasing of FFV as shown in Figures 3(c) and (d), which is consistent with the wide accepted view that the increasing of FFV can supply more transport space of network for gas permeation.²⁶ Since the increasing of T_g and FFV play the combined opposite effect on increasing permeability, the prediction of the effect of side and backbone substitute group on CO₂ permeability becomes difficult.

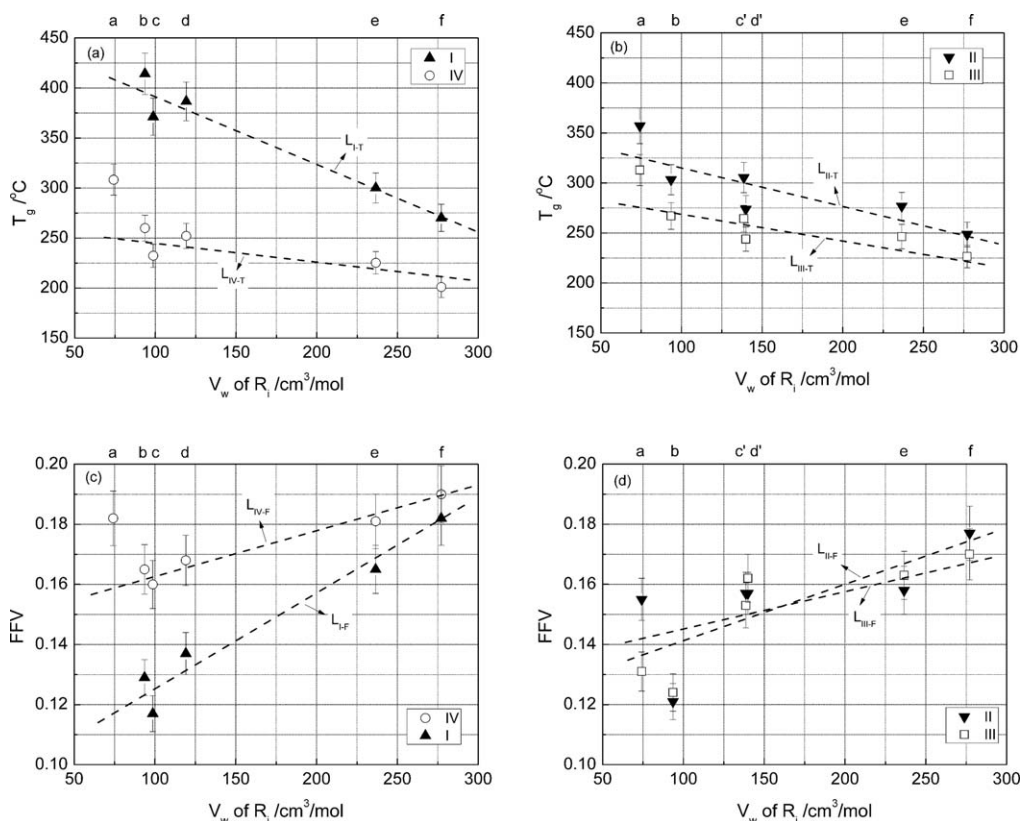


Figure 4. Relationship between (a) T_g and V_w of group I and IV, (b) T_g and V_w of group I and IV, (c) FFV and V_w of group I and IV, and (d) FFV and V_w of group I and IV.

Relationship Between T_g , FFV, and V_w

With the change of the side substitute group, some thermo-physical parameters like T_g and FFV are inevitable to be changed. Therefore, the effect of V_w of side substitute group on T_g and FFV is established by the linear fitlines of T_g-V_w and $FFV-V_w$ as shown in Figure 4. With the increasing of V_w of side substitute group in the four groups of PI polymers, T_g simply decreases as shown in Figures 4(a,) and (b) while FFV increases as shown in Figures 4(c) and (d). Actually, the decreasing trend of T_g is helpful to increase the mobility of the polymer chain, which is associated with the reports that the T_g of glassy polymers is decreased due to the introduction of large substitute groups.²⁶ The increasing range of FFV is over 0.02–0.06, which means more transport space generated among polymer network.¹⁸

Besides, the calculated slopes of the linear fitlines based on eqs. (1) and (2) are summarized in Table II. From group I to IV, the slopes of T_g-V_w increase from -0.68 to -0.2 , indicating that the increasing V_w of backbone substitute group can much effectively reduce the T_g of PI polymers than the smaller ones. By contrast, the slopes of $FFV-V_w$ almost keep stable at the range from 0.0001 to 0.0003, suggesting that the increasing V_w of backbone substitute group can slightly increase the FFV of PI polymers. It can be seen that the decreasing of T_g and the increasing of FFV can play both positive effects on improving permeability with the increasing of V_w of side substitute group.

Relationship Between Permselectivity and V_w of Side Substitute Groups

The linear fitlines of permeability and selectivity to V_w of side substitute group as the intermediate parameter are shown in Figure 5. To obtain the exact fitlines, the side substitute group that can cause larger derivation than other ones is ignored during the calculation, such as the side substitute group *a* in group I and the side substitute group *c'* in group II. The results show that the CO_2 permeability simply increases as shown in Figure 5(a,b) and the CO_2/N_2 selectivity decreases as shown in Figure 5(c,d), when the V_w of side substitute group increases from *a* to *f*. In our work, such kind of opposite trend between permeability and selectivity of PI polymers still obeys the trade-off relationship as found by Robeson et al.²

The calculated slopes of the linear fitlines based on eqs. (1) and (2) are summarized in Table II, where the correlation coefficients of the linear fitlines are about 0.87–0.99. The slopes of fitlines are divided into two types, positive and negative value. It can be found that the slopes of $P-V_w$ are positive, indicating the promotion function of V_w of side substitute group on improving the CO_2 permeability. Specially, when the V_w of the backbone substitute group increases from $93.57 \text{ cm}^3/\text{mol}$ (group I) to $184.21 \text{ cm}^3/\text{mol}$ (group IV), the slopes of $P-V_w$ decline sharply from 0.11 to 0.003, suggesting that the large backbone substitute group significantly slow down the growth trend of CO_2 permeability. Besides, the slopes of $S-V_w$ are negative, displaying the weakened function of V_w of side substitute group on

Table II. Slopes of Linear Fitlines Calculated with Permselectivity and Thermophysical Property

Group	V_w of backbone substitute group (cm^3/mol)	k			
		$T_g - V_w^*$	$\text{FFV} - V_w^*$	$P - V_w^*$	$S - V_w^*$
I	93.57	-0.68	0.0003	0.11	-0.009
II	134.76	-0.4	0.0002	0.027	-0.027
III	146.16	-0.25	0.0001	0.017	-0.033
IV	184.21	-0.2	0.0002	0.003	-0.019

reducing the selectivity. It needs to be noted that the slopes of $S - V_w$ first decrease from -0.009 (group I) to -0.033 (group III), and then increase to -0.019 (group IV). Obviously, the increasing V_w of backbone substitute group suppress the decline of selectivity than the smaller ones. Additionally, the decline of selectivity of group IV with the largest backbone substitute group is inhibited slightly due to special interaction between F atoms and CO_2 .³³

To distinguish the validity of the various established relationships, the CO_2 permeability of PI polymers with pp'MDA and 3,6-diaminocarbazole (CDA) as side substitute groups shown in Figure 5 is predicted by the linear fitlines based on T_g , FFV, and V_w of side substitute group. The predicted CO_2 permeability is summarized in Table III. Compared with the experimental CO_2 permeability of 2.17 and 17.1 barrer in the reported literature,³¹ it can be found that the predicted CO_2 permeability based on $P - V_w$ relationship is much closer to the reported experimental data than other predicted ones, verifying the effectiveness of the relationship of $P - V_w$.

Effect of V_w of Backbone Substitute Group on Permselectivity and Thermophysical Parameters

In addition to the effect of V_w of side substitute group on permselectivity of PI polymers, the effect of V_w of backbone substitute group on the performance of PI polymers are qualitatively analyzed using 2,2-bis(4-aminophenyl)hexafluoropropane (BAPHF) and 2,2-bis(4-trifluoromethyl-3-aminophenyl)hexafluoropropane (BATPHF) as the fixed side substitute groups. It should be noted that the V_w of BAPHF and BATPHF are 236.56 and 277.12 cm^3/mol , respectively. They are considerably larger than the four kinds of backbone groups in volume. Therefore, the effect of V_w of backbone group on CO_2 permeability can be thoroughly reflected. The linear fitlines of $T_g - V_w$, $\text{FFV} - V_w$, $P - V_w$, and $S - V_w$ are shown in Figure 7. It is interesting to find that T_g exhibits a simple decreasing trend with the increasing V_w of backbone substitute group as shown in Figure 7(a). This indicates that the increasing V_w of backbone group can efficiently reduce the T_g , which is similar to that of the side substitute group as discussed in Section relationship between permeability and V_w of side

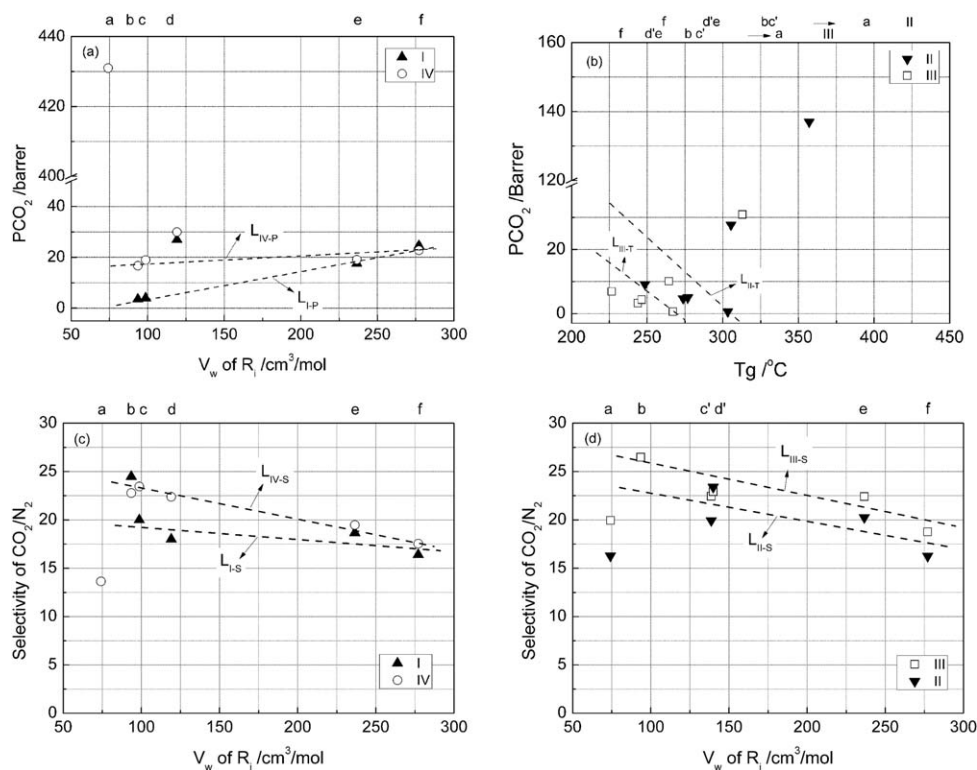


Figure 5. Relationship between (a) P and V_w of group I and IV, (b) P and V_w of group II and III, (c) S and V_w of group I and IV, (d) S and V_w of group II and III.

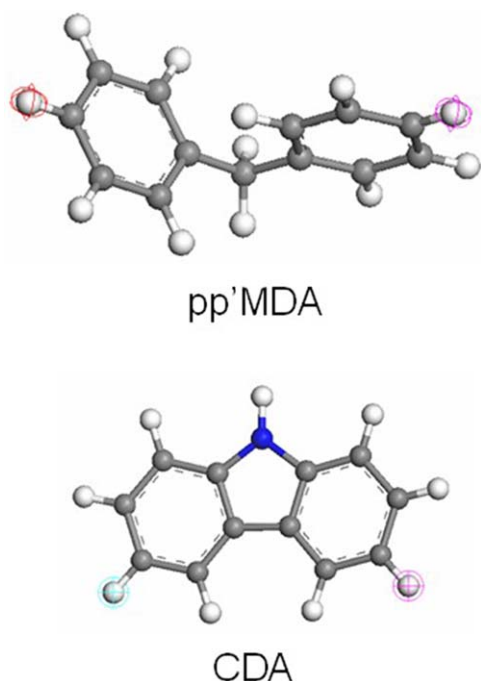


Figure 6. Basic structure of side substitute group pp'MDA and CDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

substitute groups. By contrast, FFV first decreases from the point of group I–II then increase from the group II–IV with the increasing V_w of backbone substitute group as shown in Figure 7(b). This

Table III. Comparison of the Experimental and Predicted CO_2 Permeability

Polymer	V_w of $R_i/\text{cm}^3/\text{mol}$	PCO_2 [30]/bar	PCO_2 (predicted)		
			$P-V_w$	$P-T_g$	$P\text{-FFV}$
II-pp'MDA	98.68	2.17	2.58	6.44	4
IV-CDA	85.7	17.1	17.15	9.89	21

suggests that the increasing V_w of backbone substitute group cannot simply increase FFV, which is different with that of the side substitute group as discussed in Section relationship between permeability and V_w of side substitute groups. Correspondingly, the CO_2 permeability of group IV with the large backbone substitute group that breaks the single decreasing trend with increasing V_w of backbone substitute groups but pushes the permeability to the level of group I as shown in Figure 7(c). This is due to the competition of FFV over T_g resulting in the increasing trend of permeability from group III to IV. The selectivities of CO_2/N_2 and CO_2/CH_4 also increases first and then lead to the slightly higher position than that of group I as shown in Figure 7(d). Moreover, PI-BAPHF polymers have generally higher T_g but lower FFV than that of PI-BATPHF as shown in Figure 7(a,b). This is due to the smaller V_w of BAPHF than that of BATPHF, which is consistent with the increasing V_w of side substitute group leading to the decreased T_g and increased FFV. Combined with the double effect of lower T_g but higher FFV, the CO_2 permeability of the PI-BAPHF polymers is higher than that of the PI-BATPHF polymers as shown in Figure 7(c,d). Among the four kinds of

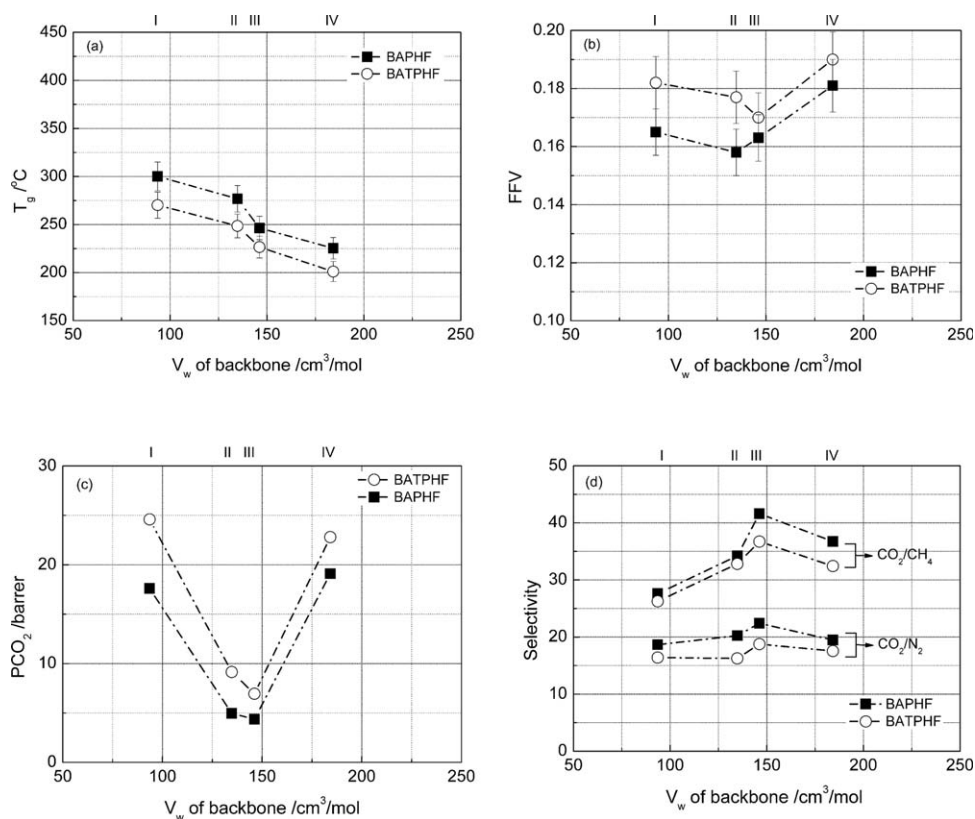


Figure 7. Relationship between (a) T_g and V_w , (b) FFV and V_w , (c) P and V_w , and (d) S and V_w .

backbone substitute group, group IV with the largest backbone substitute group plays a comparable positive effect on improving permeability and maintain a slight increasing of selectivity.

CONCLUSIONS

V_w was introduced as a quantitative parameter to bridge the relationship between thermophysical parameters of substitute group and performance property of PI polymers. On one hand, the V_w of side substitute group increases with the increasing of total atom number of side substitute groups. Conversely, the ΔV_w of both backbone substitute group and the whole PI polymer is enlarged owing to the huge volume difference of the backbone substitute groups being changed from flat to stereo structure. Instead of the single linear trend between permeability and T_g or FFV, the linear fitline of $P-V_w$ can predict the relationship between thermophysical parameters and performance property and is well verified by two kinds of side substitute groups. The positive slopes of $P-V_w$ indicate the effect of the increasing V_w of side substitute group on improving CO_2 permeability. Besides, the decreased slopes of $P-V_w$ exhibit the effect of large backbone substitute group on inhibiting the growth of CO_2 permeability. Different to the single increasing effect of V_w of side substitute group on CO_2 permeability, the increasing V_w of backbone substitute group results in the CO_2 permeability first decreasing then recovering to the original and lower level, with a slight increasing of selectivity being achieved.

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