

Factors Defining the Selectivity Polymer Membranes: A Fractal Model

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ABSTRACT: It is shown that the selectivity of the polymer nonporous membranes by the diffusivity depends on the polymer structure by rather complex way. The most important characteristic in this case is the dimension D_t controlling the gas transport processes and the molecular mobility degree influences only at large enough values of diameter of

the selected gas molecules, the difference of these diameters and the dimension D_t . © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 331–333, 2006

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INTRODUCTION

It was repeatedly assumed earlier that the selectivity of polymer membranes by the coefficients of gas permeability¹ and the diffusion² depends on the chain kinetic rigidity. In favor of such assumption several confirmations were cited, but the direct correlation between these properties of polymers is absent. The purpose of the present article is to determine the factors influencing the selectivity of polymer membranes and to give the quantitative description of this influence in the terms of a fractal model.

EXPERIMENTAL

For the calculation of a coefficient of the separation of gases i and k by diffusivities α_{ik}^D , the diffusivities D by He and CH₄ for polyvinyltrimethylsilane (PVTMS) and polydimethylsiloxane (PDMS) and the equation of type Arrhenius are used³:

$$D = D_0 e^{-E_D/RT} \quad (1)$$

where D_0 is a constant, E_D is diffusion activation energy, R is a universal gas constant, T is the testing temperature, for the calculation of D temperature dependence in interval $T = 293$ – 420 K in case of the diffusion of C₂H₄ and C₃H₈ in PVTMS.⁴ The values of a molecule diameter d_m for the used gases (He, CH₄,

C₂H₄, and C₃H₈) are accepted according to the data of papers.^{3,5}

RESULTS AND DISCUSSION

As it is known,⁶ the part of a polymer chain in the amorphous phase between the points of macromolecule topological fixation (entanglement nodes, crosslinks, etc.) is a fractal with dimension D_{ch} ($1 < D_{ch} \leq 2$). The value of D_{ch} is a characteristic of the chain rigidity or, more exactly, of molecular mobility degree. Khalikov and Kozlov⁷ received the following analytical relationship between D and D_{ch} :

$$D = KD_{ch}^\Delta \quad (2)$$

where K and Δ are constants for each gas penetrant.

It was also found that the values K and Δ for PVTMS are the function of gas-penetrant molecule diameter d_m and are determined as⁷

$$K = 0.39d_m^{-12.5} \quad (3)$$

$$\Delta = 1.94 \times 10^{-4}d_m^{6.25} \quad (4)$$

If the values of d_m are accepted in Å, then D , according to the eq. (2), is received in units cm²/s. Within the framework of a fractal model of gas transport the value of D is determined as follows⁸:

$$D = D_0' f_g (d_n/d_m)^{2(D_t-d_s)/d_s} \quad (5)$$

where D_0' is a universal constant, f_g is a relative free volume, d_n is a diameter of the microvoid of this

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volume, D_t is the dimension controlling the processes of gas transport, d_s is a spectral dimension of the polymer structure (further it is accepted equal to 1.0).

As it is shown before,⁹ for PVTMS the exponent in the eq. (5) is equal to 12.5. Therefore, comparing this value with the exponents in the eqs. (3) and (4), it can be written that

$$K = 0.39d_m^{-2(D_t-d_s)/d_s} \quad (6)$$

$$\Delta = 1.94 \times 10^{-4}d_m^{(D_t-d_s)/d_s} \quad (7)$$

The checking of this assumption will be made later. Entirely the equation for the determination of a selectivity coefficient of two gases i and k by the diffusivity α_{ik}^D can be written as follows

$$\alpha_{ik}^D = \left(\frac{d_{m_i}}{d_{m_k}}\right)^{-2(D_t-d_s)/d_s} D_{ch}^{1.94 \times 10^{-4}(d_{m_i}^{(D_t-d_s)/d_s} - d_{m_k}^{(D_t-d_s)/d_s})} \quad (8)$$

for $d_{m_i} < d_{m_k}$.

It is necessary to mention the important feature of the eq. (8): the dimension D_{ch} influences on value α_{ik}^D only at large enough absolute values d_{m_i} and d_{m_k} , difference ($\alpha_{m_i} - \alpha_{m_k}$) and dimension D_t . At small values of these parameters, the exponents for D_{ch} in the eq. (8) is less than one and the molecular mobility effect in this case is sharply decreased (the second multiplier of the equation is approaching to one).

The influence of the molecular mobility characterized by dimension D_{ch} can be followed most simply on the example of D temperature dependence since the D_{ch} increase at T raising is well known.⁶ The value of D_{ch} as function T can be theoretically calculated as follows. The relative fraction of the local order regions (clusters) φ_{cl} can be determined according to the next percolation relationship⁶

$$\varphi_{cl} = 0.03(T_{cr} - T)^{0.55} \quad (9)$$

where T_{cr} is a critical temperature, equal to the glass transition temperature T_g for the amorphous polymers and the melting temperature T_m , for the semicrystalline polymers.

Then the following simple relationship⁶ can be used

$$\frac{2}{\varphi_{cl}} = C_{\infty}^{D_{ch}} \quad (10)$$

where C_{∞} is a characteristic ratio, which is the indicator of the statistical flexibility of chain¹⁰ and is equal to ~ 4 for PVTMS.⁹

The comparison of the experimental (where the values of D were calculated according to the eq. (1)) and the estimated according to the eq. (8) α_{ik}^D values for PVTMS as function of D_{ch} is shown in Figure 1. As a

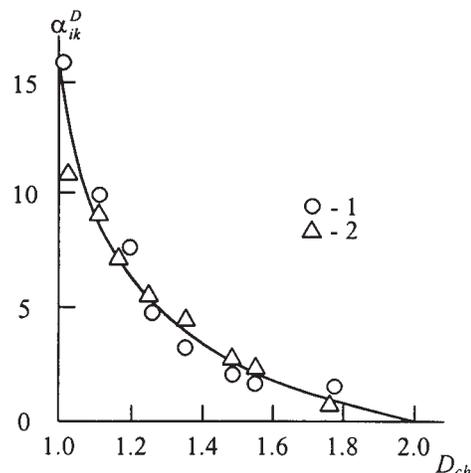


Figure 1 The dependences of selectivity coefficient CH_2 and C_3H_8 by diffusivity α_{ik}^D on fractal dimension of a chain part between the entanglements D_{ch} for PVTMS. The calculation according to the eq. (1) (1) and eq. (8) (2).

gas i C_2H_4 is supposed and as a gas k , C_3H_8 . As one can see, the good correspondence of α_{ik}^D values calculated by both mentioned methods is observed. As it is assumed,^{1,2} the increase of D_{ch} results to α_{ik}^D decrease and at $D_{ch} \approx 1.50$ the inversion of D values is observed: the value of D for C_3H_8 becomes bigger than the corresponding value for C_2H_4 . Therefore, the plot of Figure 1 clearly confirms the thesis about the selectivity decrease at raising the molecular chain mobility.

As it is known,³ PVTMS and PDMS have large enough D values, but sharply differing coefficients of the selectivity. So, the value of α_{ik}^D for He and CH_4 in the PVTMS case is equal to ~ 206 and in the PDMS case, about 4.8.³ The eq. (8) allows to explain this difference. The parameters of this equation in the PVTMS case are equal to: $2(D_t - d_s)/d_s = 12.5$, $D_{ch} = 1.046$. For PDMS the following magnitudes are obtained: $2(D_t - d_s)/d_s = 3.8$, $D_{ch} = 1.8$. Then the calculation according to the eq. (8) gives the following values: $\alpha_{ik}^D = 328$ for PVTMS and 6 for PDMS, that is corresponded with the experimentally obtained values of this parameter. It is important that in this case the α_{ik}^D value is independent on D_{ch} (for PVTMS because of the small value D_{ch} and for PDMS because of the small value D_t), but is entirely defined by D_t difference: 7.25 for PVTMS and 3.8 for PDMS. It is necessary to mention that in virtue of the condition $d_{m_i} < d_{m_k}$ the D_{ch} increase will decrease α_{ik}^D .

The eq. (8) also allows to predict the α_{ik}^D for the various polymers and the gas pairs according to the following technique. In the study of Khalikov and Kozlov¹¹ the D_t increase at $T_g(T_m)$ raising was shown and the corresponding calibrating plot is adduced, allowing the estimation of exponents in the eq. (8). In Figure 2 the comparison of the experimental^{3,12} and calculated according to the eq. (8) α_{ik}^D values for 12

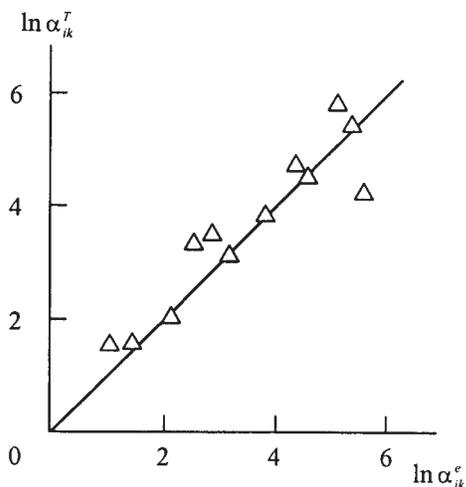


Figure 2 The comparison of the experimental α_{ik}^e and calculated according to the eq. (8) α_{ik}^T selectivity coefficient H_2 and CH_4 for 12 polymers in double logarithmic coordinates.

polymers by H_2 and CH_4 is shown. As for these gases the d_m and $(d_{m_i} - d_{m_k})$ are relatively small, then D_{ch} influence becomes appreciable only at large enough D_t ($D_t > 5.0$). As one can see even in this simple variation good enough correspondence of the theory and the experiment (the average discrepancy is equal to $\sim 27\%$) is obtained, though the experimentally determined α_{ik}^D values can have the essential scatter. So, for PVTMS the value of α_{ik}^D for the pair H_2 – CH_2 is equal to 178 according to the data of paper¹² and to 261 according to the data of a previous work,³ i.e., the discrepancy is about 32%. Therefore, we can believe that the accuracy of the theoretical prediction according to the eq. (8) is about equal to the experiment error. This correspondence also confirms the correctness of the choice of exponents in the eqs. (6) and (7).

And in the conclusion it is necessary to mention one important theoretical aspect. As follows from the earlier cited estimations, D_t value influences on the polymer selectivity much more strongly than D_{ch} . In its turn, as D_t either fractal (Hausdorff) dimension of structure d_f or dimension of the areas of localization of the excessive energy D_f can be used depending on the mechanism of gas diffusion.¹³ These dimensions are connected between themselves by the relationship¹⁴

$$D_f = 1 + \frac{1}{3 - d_f} \quad (11)$$

and in its turn the value of d_f is determined according to the following equation⁶

$$d_f = 3 - 6 \left(\frac{\varphi_{cl}}{C_\infty S} \right)^{1/2} \quad (12)$$

where S is the cross section of a macromolecule in units of Å.

Hence, the dimension D_t (d_f or D_f) is determined by the characteristics both molecular (C_∞ and S) and supermolecular (φ_{cl}) structure of polymer. It can be expected, as the polymer is a thermodynamically non-equilibrium solid and for its description, as minimum, two order parameters¹⁵ are required.

CONCLUSIONS

Therefore, the results of the present article showed that the selectivity of the polymer nonporous membranes by the diffusivity depends on the polymer structure by rather complex way. The most important characteristic in this case is the dimension D_t and the molecular mobility degree influences only at large enough values of diameter of the selected gas molecules, the difference of these diameters and the dimension D_t .

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