# Kinetic free volume controlled gas separation properties of glassy polyheteroarylenes

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It is argued that gas separation properties (in particular, selectivity) of glassy polymers are better correlated with the kinetic free volume fraction, $f^K = 1 - K_a/K_c$, rather than with the geometrical counterpart, $f^G = 1 - K_a$ (where $K_a$ and $K_c$ are the molecular packing coefficients in the amorphous and crystalline states, respectively).

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In membrane science, selectivity ($\varphi^{A/B}$) serves as a measure of the efficiency of separation of gas A from the binary gas mixture A + B. By definition, total selectivity $[\varphi^{A/B} = K^A/K^B = (D^A/D^B)(S^A/S^B)]$ is a product of two contributions which may be identified as the kinetic and thermodynamic selectivities, respectively ($K^i$, $D^i$ and $S^i$ are the permeability, diffusivity and solubility of $i$ gas in and through the membrane). The latter depends on the poorly defined 'affinity' between penetrant molecules and membrane material, while the former is believed to be free volume controlled.

It is the purpose of this communication to explore the possibility of a correlation between selectivity and a properly defined free volume of a glassy polymer (rubbery polymers were deliberately omitted from the analysis since, as a general trend, their selectivity is orders of magnitude smaller as compared to the majority of polymeric glasses[1]).

Basically, the free volume fraction of an amorphous substance is defined as

$$f = (V - V^*)/V = 1 - V^*/V \qquad (1)$$

where $V$ is the molar volume and $V^*$ is the occupied volume. Substitution of the intrinsic (or van der Waals) molecular volume, $V_i$, for $V^*$ in equation (1) yields the so-called geometrical free volume fraction:

$$f^G = 1 - K_a \qquad (2)$$

where $K_a = V_i/V$ is the molecular packing coefficient of the amorphous substance. As can be seen from *Table 1*[2], the values of $K_a$ for a series of polyamideimides are nearly the same and thus cannot account for the variation of selectivity for a helium/carbon dioxide pair ($\varphi^{He/CO_2}$).

Implicit in the application of equation (2) was the assumption that the total free space between impenetrable van der Waals molecular cores in a 'structureless' membrane material is equally accessible to the diffusion of gas molecules. However, this assumption is inconsistent with the experimental evidence of the effect of morphology on gas transport properties of crystalline polymers[3,4], microphase-separated block copolymers[5] and segmented polyurethanes[6] according to which crystalline regions in crystalline polymers and densely packed (crystal-like) domains in segmented polyurethanes are impenetrable to gas molecules. Structural microheterogeneity with alternating regions of dense and loose molecular packing is also a characteristic feature of one-component, glassy substances in which thermal density fluctuations are effectively 'frozen in' as the molten substance is cooled through and below the glass transition interval[7,8].

It follows therefore that a more appropriate choice for $V^*$ in equation (1) would be the molar crystalline volume, $V_c$, which defines the kinetic free volume fraction:

$$f^K = 1 - K_a/K_c \qquad (3)$$

where $K_c = V_i/V_c$ is the molecular packing coefficient of a crystal. The validity of this proposal may be assessed from plots of the frequencies of statistical occurrence (i.e. histograms) of values of $K_a$ and $K_c$ for a large number of flexible chain polymers (*Figure 1*)[9]. It can be seen that in contrast to a fairly narrow $K_a$ histogram with a peak centred at the 'universal' value $K_a = 0.68$, the values of $K_c$ spread over a much wider interval spanning from 0.60 to 0.85. In view of equations (2) and (3) this means that the $f^G$ is a poor choice compared to $f^K$, with respect to the possibility of rationalizing the differences in gas separation properties of various glassy polymers.

The values of $f^K$ may be calculated in a straightforward manner by a simple substitution of $K_a/K_c = V_c/V_a$ into equation (3). In those cases when the crystallographic density of a polymer is unavailable, the following empirical equation may be used[7]:

$$K_c = [1 + 0.127(a/\sigma)]^{-1} \qquad (4)$$

**Table 1** Selected properties of polyamideimides

| Polymer | $K_a$ | $d_\perp$ (Å) | $\langle l \rangle$ (Å) | $\varphi^{He/CO_2}$ |
|---|---|---|---|---|
| 1 | 0.687 | 5.20 | 8.65 | 1.56 |
| 2 | 0.663 | 5.50 | 7.51 | 2.73 |
| 3 | 0.683 | 5.82 | 7.60 | 1.96 |
| 4 | 0.686 | 5.40 | 7.49 | 4.86 |
| 5 | 0.688 | 5.35 | 6.92 | 1.66 |
| 6 | 0.687 | 5.16 | 5.46 | 4.85 |

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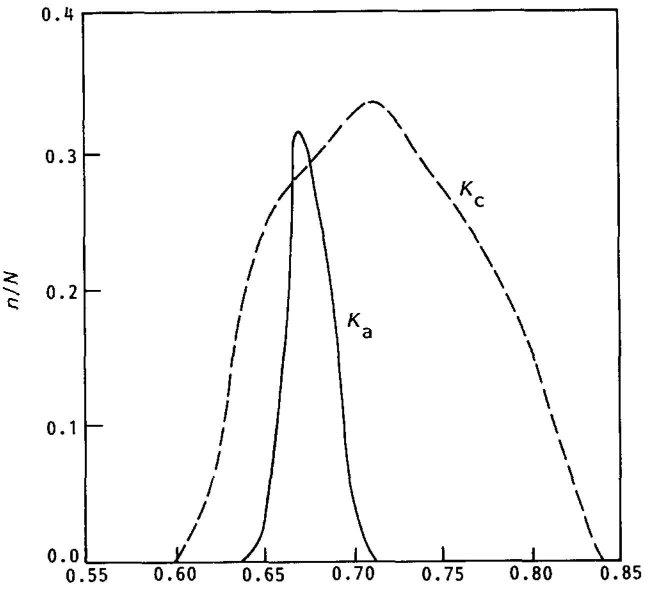

**Figure 1** Histograms of packing density coefficients in the amorphous ($K_a$) and crystalline ($K_c$) states for flexible chain polymers[9]

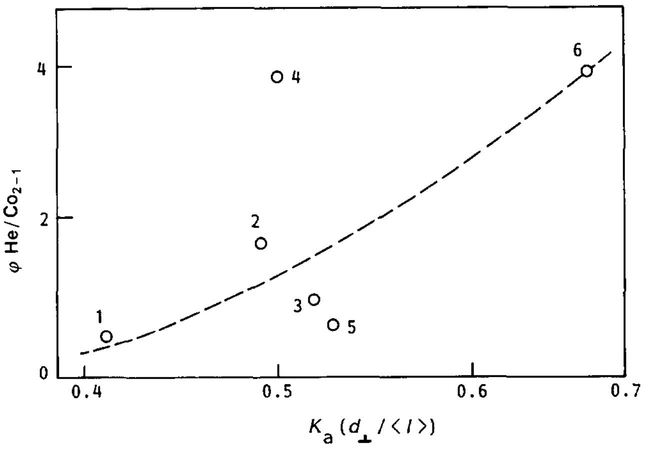

**Figure 2** Dependence of the selectivity parameter for the He/CO$_2$ gas pair ($\varphi^{\mathrm{He/CO_2}}$) on $K_a$ $(d_\perp/\langle l\rangle)$ for polyamideimides

where $\sigma$ is the intrinsic chain stiffness parameter (steric factor), $a \cong A^{1/2}$ is the chain thickness and $A$ is the chain cross-sectional area (usually estimated from the crystalline unit cell dimensions).

Assuming that equations (3) and (4) also apply in the case of semi-flexible chain polymers, one should expect a correlation between $\varphi^{A/B}$ and $K_a$ $(a/\sigma)$ for polyamideimides. For this polymer series the values of the interplanar distance, $d_\perp$, from wide-angle X-ray diffraction[10] may be substituted for $a$, and chain persistence length[2,11], $\langle l\rangle$, for $\sigma$.

As can be seen from the plot of $\varphi^{\mathrm{He/CO_2}}$ *versus* $K_a(d_\perp/\langle l\rangle)$ (*Figure 2*), there is a fair correlation between the quantities (broken line) with a single exception (point 4) which cannot be immediately rationalized. Nevertheless, even these very limited data seem sufficient to justify the use of $f^K$ as an appropriate parameter to discuss the influence of molecular architecture, as embodied in equation (4), on the gas separating properties of glassy polymers.

In this respect, the relevance of this approach to recent papers by Petropoulos[1], Stern *et al.*[12] and Koros *et al.*[13] is especially illuminating. Obviously, $f^K$ is controlled not by a single molecular parameter, namely, interchain spacing $d_\perp$, as claimed in references 1, 12 and 13, but rather by a characteristic ratio of $d_\perp$ and the other fundamental molecular parameter, the chain persistence length $\langle l\rangle$. Work is now in progress to test this idea on a wider range of glassy polymers.

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