The Dependence of Diffusivity of Hydrocarbons in Polyvyniltrimethylsilane on Molecular Mobility Level

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ABSTRACT: It is shown that the diffusivity value of various gases in polyvinyltrimethylsilane is controlled by two factors: molecular mobility level, characterized by fractal dimension of chain part between entanglements, and the size of gas-penetrant molecule. Very strong power dependence of diffusivity on both these factors, explaining very large variation of diffusivity for limited interval of mentioned dimension, is obtained. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4048–4050, 2006

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INTRODUCTION

At present it is supposed that the rigidity increase of polymer chain and, consequently, molecular mobility reduction results in the decreasing of polymer's diffusivity D.[1] Most vividly this effect is expressed in temperature dependence D: an increase of testing temperature and, consequently, molecular mobility amplification results in substantial growth D.[2] As it is known,[3] within terms of fractal analysis a molecular mobility degree can be characterized quantitatively by fractal dimension D_{ch} of chain part between points of its topological fixation (entanglements nodes, crosslinks, and so on). Authors have found very strong dependence of D on D_{ch} in the case of high density polyethylene (HDPE), expressed by the following relationship:

$$D = 7.66 \times 10^{-14} D_{ch}^{28.1} \qquad (1)$$

where D is given in cm^2/s.

The purpose of the present article is to study the dependence of diffusivity on molecular mobility level for polyvinyltrimethylsilane (PVTMS) within terms of fractal model, using temperature dependence D for four hydrocarbons.[4]

EXPERIMENTAL

The experimental values of diffusivity of 13 gases in PVTMS are used.[5–7] Experimental temperature dependences D for hydrocarbons C_2H_4 and C_3H_8 were calculated according to the Arrenius equation:

$$D = D_0 \, e^{-E_D/RT} \qquad (2)$$

where values of constant D_0 and diffusion activation energy ED were adopted according to the data of paper[5] (R is universal gas constant, T is testing temperature). The dependence $D(T)$ was calculated in interval T = 293–403 K. The values of diameter d_m of gas-penetrant molecules are given in literature.[6,7] The glass transition temperature T_g for PVTMS is equal to 440 K.[8]

RESULTS AND DISCUSSION

As mentioned above, within terms of fractal analysis, a molecular mobility degree can be characterized by dimension D_{ch}, which is estimated according to the eq. (3)

$$\frac{2}{\varphi_{cl}} = C_x^{D_{ch}} \qquad (3)$$

where φ_{cl} is relative fraction of local order domains (clusters), C_∞ is characteristic ratio, for PVTMS, equal to 4.0.[9]

In its turn, the value φ_{cl} as a function of T is determined according to the following percolation relationship:[3]

$$\varphi_{cl} = 0{,}03(T_g - T)^{0{,}55} \qquad (4)$$

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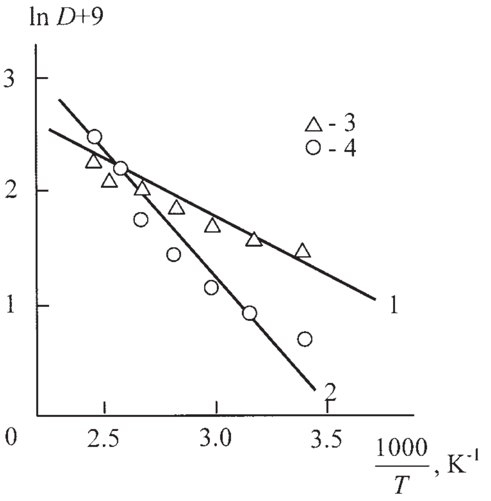

Figure 1 The dependence of diffusivity D on reciprocal value of testing temperature T for diffusion of C_2H_4 (1,3) and C_3H_8 (2,4) in PVTMS in logarithmic coordinates. The calculation made according to the eq. (2) (1,2) and eqs. (5)–(7).(3,4)

The eqs. (3) and (4) allow the calculation φ_{cl} and, consequently, D_{ch} only on the basis of known basic characteristics of polymer: T_g and C_∞, which characterize statistical flexibility of polymeric chain.[10]

It was found that in interval $T = 293–403$ K , D_{ch} is observed to increase systematically in limits 1046–1590, concurrent with growth D. This allows to express analytically the relationship between D and D_{ch} in the form of power function:

$$D = KD_{ch}^{\Delta} \tag{5}$$

where K and Δ are constants for every gas-penetrant.

The comparison of temperature dependences D for two gases (C_2H_4 and C_3H_8), calculated according to the eqs. (2) and (5), is shown in Figure 1. As one can see, the good correspondence of dependences $D(T)$, calculated by both methods, is obtained.

The values of constants K and Δ in the eq. (5) showed the systematic change with variation of gas-penetrant molecule diameter d_m that follows from the data of Table I. This systematic change allows to express the pointed constants with the help of the following equations:

TABLE I
The Values of Constant K and Δ in for Hydrocarbons

Hydrocarbon	d_m (Å) [5]	K	Δ
C_2H_4	4.17	1.060	1.37
C_2H_6	4.44	0.390	2.80
C_3H_6	4.99	0.137	4.18
C_3H_8	5.12	0.034	9.30

TABLE II
The Comparison of Experimental and Calculated Values of Diffusivities D for PVTMS

Gas	d_m (Å) [6,7]	D (cm²/s) Experimental [6,7]	Calculated values
He	1.78	370	1660
Ne	2.30	95	139
O_2	2.89	7.6	7.2
CO_2	3.02	5.0	4.1
N_2	3.04	3.6	3.7
CH_4	3.18	1.8	2.1
Rn	3.77	0.08	0.23
C_2H_2	3.38	0.64	0.93
C_4H_6	3.85	0.80	0.17
C_4H_{10}	5.66	0.001	0.003

$$K = 0.39 d_m^{-12.5} \tag{6}$$

$$\Delta = 1.94 \times 10^{-4} d_m^{6.25} \tag{7}$$

From the eqs. (6) and (7), very strong power dependence of K and Δ (and, consequently, diffusivity) on d_m is observed. Analogous strong dependence $D(d_m)$ is confirmed experimentally: so, at transition from He ($d_m = 1.82$ Å) to C_4H_{10} ($d_m = 5.66$ Å), the value D in case PVTMS is decreased almost on 6 orders.[6,7]

For check up of generality of the relationships[5–7] was made the calculations of D according to the relationships for PVTMS and 10 gases and penetrants, whose d_m values are changed in the abovementioned interval ($d_m = 1.82–5.66$ Å). The comparison of experimental results [6,7] and those calculated by the pointed method diffusivities for PVTMS is shown in Table II. As one can see, in spite of a substantial error for some gases (for example, He), the calculation gives correct measurement interval D at $T = 293$ K, namely, on 6 orders of magnitude. In common case, such error is due to the power form of relationships themselves[5–7] and large values of exponents in them.

CONCLUSIONS

Thus, the results of the present communication have shown that the value of diffusivity of various gases in polyvinyltrimethylsilane is controled by two factors: molecular mobility level, characterized by fractal dimension D_{ch}, and gas-penetrant molecule size. As in the case of HDPE (eq. (1)), very strong power dependence of D on both the abovementioned factors is obtained, explaining very large variation in D for the limited intervals of change $D_{ch} = 1.046–1.590$ and $d_m = 1.82–5.66$ Å.

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