

The Diffusion of Gases in Semicrystalline Polyethylene and Its Melt

G. V. Kozlov, G. E. Zaikov

Institute of Biochemical Physics Russian Academy of Sciences, Kosygin st. 4, 119991, Moscow, Russia

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ABSTRACT: The fractal analysis and the cluster model of the polymer amorphous structure make it possible to account for a change in the diffusion coefficient in polyethylene both above and below the melting temperature. The proposed interpretation explains the diffusivity jump at the melting point as resulting from the disintegration of local-

order regions. The formation of these regions is due to polyethylene crystallization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3761–3763, 2004

Key words: polyethylene; melt; diffusivity; fractal analysis; cluster model; degree of crystallinity; thermal cluster

INTRODUCTION

The existence of a jump in the diffusivity D at the polyethylene (PE) melting point T_m is a well-known experimental fact.¹ The theoretical model suggested in ref. 1 describes the temperature dependence of D , which assumes two different equations for the $T < T_m$ and $T > T_m$ temperature ranges. However, this model does not allow for the structural differences between the amorphous phases of PE in the semicrystalline ($T < T_m$) and viscous ($T > T_m$) states.

The aim of this work was to demonstrate the possibility of describing the $D(T)$ dependence, including the D jump at T_m , in terms of a single model, which takes into account the aforementioned structural differences. The methods of fractal analysis² and the cluster model of the polymer amorphous state³ were used for this purpose.

RESULTS AND DISCUSSION

The main equation in the fractal model of gas transport in polymers, which was proposed in ref. 2, is

$$D = D_0 f_f (d_h / d_m)^{2(D_f - d_s) / d_s} \quad (1)$$

where D_0 is a constant, f_f is the relative free volume, d_h is the diameter of a microvoid of this volume, d_m is the diameter of a penetrant gas molecule, D_f is the dimension of the excess energy localization regions, which controls the gas transport processes in polymers, and d_s is the spectral (fractal) dimension.

Let us define the quantities included in eq. (1). In this work, D_0 is a fitting parameter, which is different for the $T < T_m$ and $T > T_m$ temperature ranges, in accordance with the classical ideas on gas diffusion in polymers.^{1,4} The f_f value in terms of the model advanced in ref. 3 is proportional to the relative amount φ_{lm} of the loose-packed matrix and may be estimated from the simple relationship⁵

$$f_f = 0.113 \varphi_{lm} \quad (2)$$

where the factor 0.113 corresponds to the viscous state of PE.⁶

The d_h values may be calculated from the experimental values of free-volume microvoids for high-density polyethylene (HDPE), which were found by using positron spectroscopy⁷ under the assumption that such a microvoid is simulated by a three-dimensional sphere. The d_m value is assumed to be constant and equal to 3.60 Å for methane, whose diffusivity was calculated according to eq. (1).⁴

The D_f value was theoretically estimated on the basis of the following reasoning. In terms of the model,³ the fraction φ_{cl} of local-order regions (clusters), which is an order parameter (in the rigorous physical meaning of the term) for the PE amorphous phase, may be defined as⁸

$$\varphi_{cl} \approx 0.03(T_m - T)^{0.55} \quad (3)$$

This equation determines the φ_{cl} value per unit volume of noncrystalline regions rather than per unit volume of the polymer. This is due to the well-known fact⁹ that gas transport takes place only in noncrystalline regions and, hence, such a calculation method is necessary for adequate comparison with experimental data for the $T > T_m$ range.

Correspondence to: G. E. Zaikov (chembio@sky.chph.ras.ru).

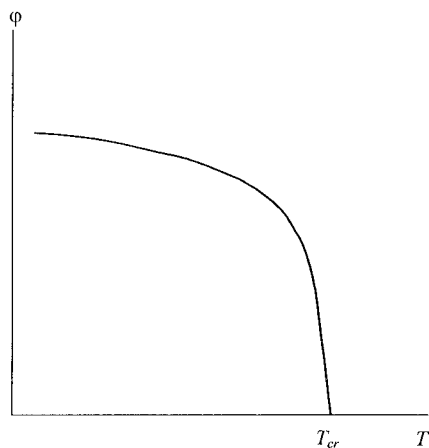


Figure 1 Schematic representation of the temperature dependence for the order parameter φ .¹⁹

The fractal dimension d_f of the PE structure can be evaluated by using¹⁰

$$d_f = 3 - 6 \left(\frac{\varphi_{cl}}{SC_\infty} \right)^{1/2} \quad (4)$$

where S is the cross-sectional area of a macromolecule, equal to $\sim 18.9 \text{ \AA}^2$ for PE,¹¹ and C_∞ is the characteristic ratio equal to 5.7 for PE.¹²

Finally, the D_f value may be determined from the expression¹³

$$D_f = 1 + \frac{1}{3 - d_f} \quad (5)$$

Since the HDPE used is a linear polymer, it is assumed to have $d_s = 1$.¹⁴

All the aforementioned estimates are correct for the temperature range $T < T_m$. As shown in ref. 7, d_h slightly increases in the $T > T_m$ range (from ~ 7.1 to 7.3 \AA over the 383–423 K interval) and the value of $f_f \sim 0.113$ is constant. Therefore, a constant value of $d_f = 2.85$ (which is typical of the rubbery polymer state¹⁰) and the corresponding value $D_f \sim 7.67$ were assumed for this range.

Let us consider the physical grounds for the appearance of a D jump at T_m in the suggested interpretation. The model developed by Tochin et al.¹ suggests that the amorphous phase may have the same structure in semicrystalline PE and in its melt. In this case, the role of the crystal phase is reduced to a decrease (proportional to the degree of crystallinity) in the D value. In addition, Tochin et al.¹ presumed that the rate-limiting step of gas diffusion in semicrystalline PE is the transport via the crystallite contact points, which should be regarded as an arbitrary assumption. It is known^{15,16} that the interface between the crystalline and the amorphous phase is the closest packed part of non-

crystalline PE regions; therefore, neither the direct contact of crystallites nor the enhanced looseness at the points of such contacts, if they do exist, should be expected.

Within the framework of the proposed interpretation, structures of the amorphous phase in semicrystalline PE and its melt differ by the presence in the former of local-order regions (clusters) that are also impenetrable by gas transport processes. The appearance of such regions at $T \leq T_m$ is due to crystallization and chain stretching in amorphous interlayers caused by crystallization.¹⁶ A certain portion of local-order regions remains at $T > T_m$, but this order will be dynamic and have a short lifetime in this case.^{17,18} The jump in the D value at T_m in terms of the most general physical concepts is due to the specificity of variation in the order parameter φ at the critical temperature T_{cr} ($T_{cr} = T_m$ for PE). Figure 1 schematically shows function $\varphi(T)$, which demonstrates a very rapid φ increase within a narrow temperature range $T \leq T_m$.¹⁹ As shown in ref. 20, function $\varphi_{cl}(T)$ can be rationalized in terms of the thermal cluster concept, where φ is defined as

$$\varphi_{cl} = \left(\frac{T_m - T}{T} \right)^{0.4} \quad (6)$$

For the D jump temperature interval adopted in ref. 1 (amounting to $\sim 5 \text{ K}$) and $T_m = 403 \text{ K}$,¹⁷ we obtain $\varphi_{cl} = 0.176$, which brings about this jump.

Figure 2 compares the experimental¹ and the calculated (according to the method described above) temperature dependence of the methane diffusivity in HDPE. As is seen, excellent agreement between the theory and the experiment is obtained; it confirms

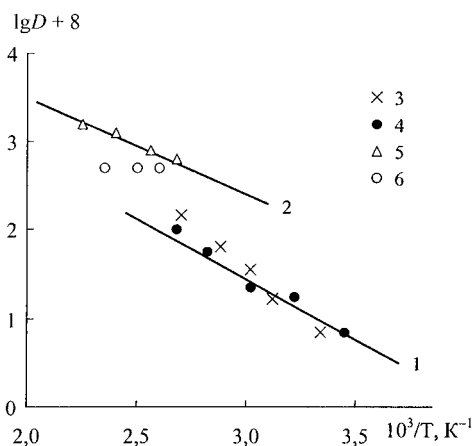


Figure 2 The temperature dependence of the methane diffusivity D in (1–3) HDPE and (4–6) its melt: (1, 2) straight lines according to data reported in ref. 1; (3, 4) points calculated according to eq. (1); and (5, 6) calculation according to eq. (7).

both the adequacy of the proposed interpretation and the correct choice of its parameters. The values of D_0 turned out to be equal to $8.1 \times 10^{-8} \text{ m}^2/\text{s}$ for $T < T_m$ and $0.84 \times 10^{-8} \text{ m}^2/\text{s}$ for $T > T_m$.

It is possible to demonstrate the physical meaning of the D jump at $T = T_m$ in an even more simple and lucid manner by using the empirical equations²¹

$$D = D'_0 e^{13\varphi_{lm}} \quad (7)$$

and

$$D = D''_0 e^{62.5f_j} \quad (8)$$

where D'_0 and D''_0 are constants.

Although eqs. (7) and (8) were derived to describe the diffusion of oxygen in some amorphous and semi-crystalline polymers,²¹ the closeness of the d_m values for O_2 and CH_4 nevertheless allow these equations to be used for preliminary estimates. For example, the $\varphi_{lm} = 1 - \varphi_{cl}$ value for $T = T_m - 5 \text{ K}$ amounts to ~ 0.828 according to the model advanced in ref. 20, whereas eqs. (4) and (5) yield $\varphi_{lm} \sim 0.933$ for $T > T_m$. Calculation according to eq. (7) yields a difference of ~ 0.61 between the $\log D$ values for these states. Such results display excellent agreement with the experimental value of the difference in $\log D$, which is equal to ~ 0.63 .¹

Figure 2 also presents a comparison between the temperature dependences for the diffusivity in HDPE and its melt as calculated according to eq. (7) and obtained experimentally.¹ The fit of the theory to the experiment is unexpectedly good, considering the approximating nature of eq. (7),²¹ and the constancy of D at $T > T_m$ is due to the condition $\varphi_{lm} = \text{const} = 0.933$ assumed above for this temperature range. It is also important that the same constant D'_0 equal to $3.65 \times 10^{-11} \text{ m}^2/\text{s}$ was used for both temperature ranges.

CONCLUSION

In summary, the methods of fractal analysis and the cluster model of the polymer amorphous state structure make it possible to explain the behavior of the diffusivity as a function of temperature within the

framework of a unified structural approach both above and below T_m . The suggested interpretation explains the jump in the D value at T_m as a result of the formation (disintegration) of the regions of local order (clusters), which are impenetrable for gas transport. The formation of clusters is due to the PE crystallization process. This interpretation provides not only a qualitative but also a quantitative description of the $D(T)$ dependence over the entire temperature range considered here.

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