

Additive Diffusion Coefficients in Polyolefins. II. Effect of Swelling and Temperature on the $D = f(M)$ Correlation

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ABSTRACT: Diffusion coefficients of a large panel of molecules were experimentally measured in virgin polypropylene at 40 and 70°C and in swollen polypropylene at 40°C. The influence of mobility increase brought out by temperature or swelling are compared. The effects are more important for high molecular weight compounds. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2434–2443, 2001

Key words: diffusion coefficient; additive; swelling; temperature; activation energy

INTRODUCTION

Additive diffusion coefficient prediction is currently a sensitive topic in the field of food and packaging interaction. The possibility of calculating migration (overestimating even when leaving a safety margin to evaluate consumer exposure) taking into account predicted diffusion coefficients and adapted diffusion models¹ is being examined widely. Calculating the maximum acceptable concentration in the material by overestimating the migration level and comparing with regulatory migration limits is what is largely aimed at.

Generally, the method to overestimate the diffusion coefficient relies on a simple parameter correlation describing the size of molecules, generally the molecular weight.²

A considerable amount of diffusion data is available for low molecular weight compounds at temperature between 20 and 40°C.

Compounds of molecular weight from 500 to 1000 are rarely studied using “pure” diffusion tests. Usually only apparent diffusion coefficients

are measured from regular tests implying contact with liquids. The results depend on potential swelling of material and interface kinetic effects (mass transfer into the liquid). In the first part of this work, the authors have presented results obtained with high molecular weight compounds at 40°C in original tests especially designed to obtain the real diffusion coefficient D_0 (without contact with liquids). These results obtained in virgin polypropylene (PP) using a large panel of molecules demonstrate a linear relationship for linear alkanes between $\text{Log}(D_0)$ and molecular weight (result already obtained for low mass compounds³). All other compounds at 40°C have lower diffusion coefficients than linear alkanes (for a given molecular weight). Considering the molecule diffusion mode and structural and geometric factors enables us to give a qualitative explanation of the difference between the diffusion of linear alkanes and other compounds.⁴

The aim of this paper is to study the evolution of the $D = f(M, \text{geometry})$ correlation when the polymer mobility is increased: *Which molecules are more sensitive to the temperature increase or the penetration of a food simulant into the material?*

The temperature effect was taken into account by Piringier²:

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$$D_p^* = 10^4 \exp \left[A_p - 0.003 M_r (45 M_r^{-1/3} - 1) - \frac{10454}{T} \right] \quad (\text{cm}^2/\text{s}) \quad (1)$$

where $A_p = A'_p - C/T$, and where M_r is the relative molecular mass of the migrant, T is the temperature in degrees K, and A'_p and C are specific parameters of the polymer matrix.

This equation leading to an overestimation of D takes into account a *constant* activation energy for a given polymer: Indeed, A_p contains a C/T term, and thus the activation energy corresponds to $R(10454 + C)$.

On the other hand, Limm and Hollifield⁵ propose the same type of relationship, but with a *variable* activation energy. They make the following assumptions:

- Linear dependence of $\text{Log}(D)$ with the molecule diameter to the power of 1.5.
- All additives have the same physical characteristics (same density and same shape factor).
- The activation energy is proportional to the diameter of the molecule. This leads to the following equation:

$$\text{Log}(D_{T,M}) = \text{Log}(D_0) + \alpha \cdot M^{1/2} - \frac{K \cdot M^{1/3}}{T} \quad (2)$$

where D_0 , α , and K are constants (independent of migrant and temperature), M is the molecular weight of additive (in g/mol), and T is temperature (in degrees K).

A variation of the activation energy in relation to the molecular weight is thus obtained. The constants of the model (calculated for PP and HDPE) were determined by experiments on migration of Irganox 1010 ($M = 1178$ g/mol) in olive oil. The model was validated by comparison with experimental migration data. However, possible swelling effects of olive oil were not discussed in Limm and Hollifield's paper. Diffusion tests involving contact of polyolefins with oils are necessarily influenced by swelling.

In this paper, the temperature effect is evaluated by a test that does not involve contact with a liquid. The swelling effect on the diffusion coefficient is evaluated by measuring D in totally swollen polymers (D_∞) (the penetration *kinetics* of the

liquid into the polymer therefore does not influence the result).

Simple mathematical equations translate the swelling effect on the diffusion of additives. The three following equations can be used⁶⁻⁸:

$$D(C) = D_0 + B \times C \quad (3)$$

$$D(C) = D_0 \times \exp(B \times C) \quad (4)$$

$$D(C) = D_0 \times \exp B \times \frac{C}{1 + C} \quad (5)$$

where C is the concentration of the substance that induces the swelling and B is a "swelling" constant.

Equations (3)–(5), which are generally applied to express autoplasmicization,⁷ are used here to account for the effect of the liquid simulant swelling on the additive diffusion.⁹

The equations expressing temperature and swelling effects on D do not reveal their physical origin. Is the increase of mobility due to a direct effect on the migrant, or is it an indirect consequence of the increase of polymer mobility?

MATERIALS AND METHODS

Diffusing Substances

The molecule panel is the same as the one studied in part I of paper [4]. It consists of linear/nonlinear alkanes, of unsaturated and/or aromatic compounds, and of different shape commercial additives. So the panel is the most likely representative of all possible shapes and functionalities (Table I).

Polymers

Model films tested were supplied by CERDATO (Lacq, France). The original amounts of additives being very low, then, do not interfere with tested diffusing substances.

- Polypropylene: 54 μm , melting point 130°C, crystallinity rate 37%.
- High density polyethylene: 67 μm , melting point 121°C, crystallinity rate 52%.
- Linear low density polyethylene: 25 μm , melting point 111°C, crystallinity rate 44%.

Table I Diffusion Coefficients (cm²/s) of Studied Molecules at 40 and 70°C in Virgin Polypropylene and at 40°C in Totally Swollen Polypropylene

	D_0 at 40°C	D_∞ at 40°C	D_0 at 70°C
Linear alkanes			
Undecane	2.1×10^{-9} ^a	1.0×10^{-8}	5.7×10^{-8}
Tridecane	2.1×10^{-9} ^a	9.0×10^{-9}	5.7×10^{-8}
Pentadecane	2.0×10^{-9} ^a	7.0×10^{-9}	5.7×10^{-8}
Hexadecane	1.3×10^{-9} ^a	5.0×10^{-9}	
Heptadecane	1.3×10^{-9} ^a	4.0×10^{-9}	
Octadecane	8.7×10^{-10} ^a	3.8×10^{-9}	4.8×10^{-8}
Docosane	2.5×10^{-10} ^a	3.0×10^{-9}	3.2×10^{-8}
Tetracosane	5.6×10^{-10} ^a	2.5×10^{-9}	
Octacosane	1.8×10^{-10} ^a	1.7×10^{-9}	2.7×10^{-8}
Hexatriacontane	2.0×10^{-11}		1.6×10^{-8}
Tetracontane	1.0×10^{-11}	2.5×10^{-10}	1.0×10^{-8}
Other molecules			
Triphenylmethane	1.3×10^{-10} ^a	6.0×10^{-10}	1.1×10^{-8}
Tetramethyl Pentadecane	4.9×10^{-10} ^a	1.2×10^{-9}	1.7×10^{-8}
Octadecanol	2.1×10^{-10} ^a		2.8×10^{-8}
Heptadecylbenzene	5.2×10^{-10} ^a	1.7×10^{-9}	
Docosanol		2.0×10^{-10}	
Squalane	9.9×10^{-11} ^a	7.0×10^{-10}	8.0×10^{-9}
Trilaurin	7.0×10^{-12}	5.0×10^{-10}	3.9×10^{-9}
Tripalmitin	from 3.0×10^{-13} to 2.0×10^{-12}	1.2×10^{-10}	2.0×10^{-9}
Commercial additives			
Tinuvin P	1.5×10^{-10} ^a	1.2×10^{-9}	3.1×10^{-8}
Chimasorb 81	1.5×10^{-10}	3.0×10^{-10}	1.4×10^{-8}
DEHP	3.8×10^{-11} ^a	4.0×10^{-10}	5.9×10^{-9}
Uvitex OB	4.1×10^{-11} ^a	1.0×10^{-10}	1.7×10^{-9}
Irganox PS800	2.0×10^{-11}	1.0×10^{-10}	1.5×10^{-8}
Irganox 1076	7.0×10^{-12}	3.0×10^{-10}	4.5×10^{-9}
Irgafos 168	from 1.0×10^{-13} to 4.0×10^{-13}	3.0×10^{-11}	7.5×10^{-10}
Irganox 1330	from 1.0×10^{-13} to 4.0×10^{-13}	6.0×10^{-11}	3.0×10^{-10}

^a Studied in previous paper.³

- Low density polyethylene: 27 μm , melting point 101°C, crystallinity rate 39%.

Swelling Liquid

The swelling liquid used for migration tests must have the following characteristics:

- a chemical structure close to official food simulants and to food fats, and
- no impurities that can react with the tested molecules or lead to coelution problems in

chromatographic analysis (this is particularly the case of the most used food simulant, olive oil, which contains many products).

First, the authors chose a mixture of C8–C12 triglycerides (Miglyol 812, Hüls) (50–5 % C8; 30–45 % C10; and less than 3% C3, C6, and C14). The advantages of this simulant are its low impurity concentration and its low average molecular weight. Thus its swelling effect would be easy to highlight (important effects). But the gas chromatography/flame ionization detector (GC/FID)

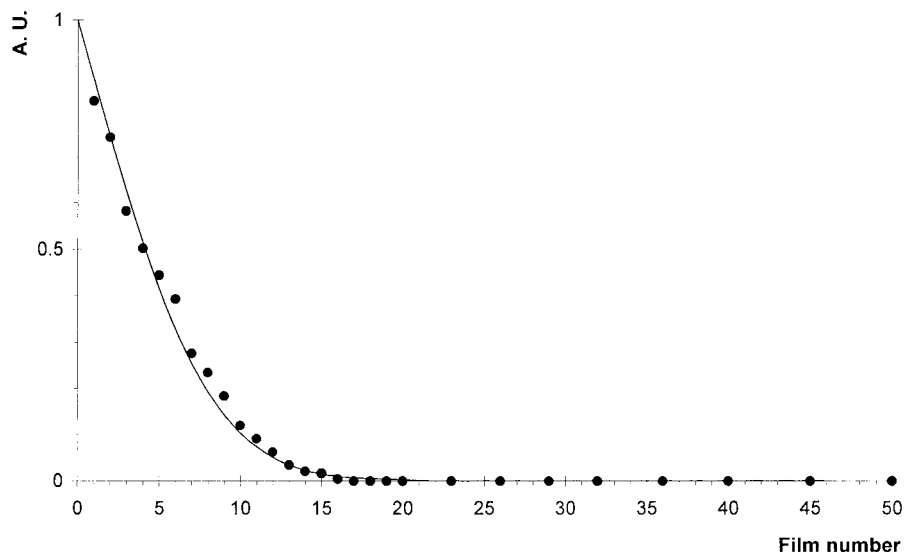


Figure 1 Diffusion profile of docosane after 26 days of contact at 40°C with a polypropylene stack (50 films of 54 μm). (●) Experimental values; (—) theoretic profile calculated with $D = 2.5 \times 10^{-10} \text{ cm}^2/\text{s}$.

analysis reveals the presence of many peaks due to the statistical arrangement of the C8 and C10 fatty acids on glyceryl.

Thus, Myglyol was replaced by glyceryl tripelargonate (triC9), which results in a single peak in GC analysis. TriC9 molecular weight is close to the average molecular weight of Myglyol; it can therefore be considered as a “Myglyol-like” pure component.

Measuring Diffusion Coefficients

Measurement of Diffusion Coefficient at 70°C

Diffusion coefficients of all molecules were measured with the stack method. Stacks of 50 films are stored at 40°C under pressure (25 kg/cm^2) for 3 days. Then the stack is put in contact with a source of additives. This source is made with PE wax (AC617A, Allied: powder, density 0.91, viscosity at 140°C 180 cps), and extracted with dichloromethane (5 mL dichloromethane/g wax; three extractions for 30 min at room temperature by immersion under stirring) in order to avoid interactions between the first layers of the stack and PE wax oligomers. The source contains three diffusing substances of the panel. The solution is made in a mold at 100°C. If the product is not highly soluble in the wax (concentration of additive used: 5%), no tests are performed. The pressure during the diffusion test is 0.5 kg/cm^2 . After a given contact time at 70°C (which has to be

adapted considering the expected diffusion coefficient) films are separated, extracted for 1 day by dichloromethane at room temperature, and the extract is then analyzed by GC/FID. The diffusion coefficient is calculated from the concentration profile in the stack thickness (Fig. 1).

Measurement of Diffusion Coefficients in a Swollen Polymer

The film is cut into disks 10 mm diameter. The samples are immersed in glyceryl tripelargonate at 40°C for 1 month until sorption equilibrium is reached (total swelling). Each sample is deposited on a metallic stick and immersed in a solution of the migrants in glyceryl tripelargonate. Concentrations of the tested substance are adapted in order to obtain about 200–2000 ppm in the film at sorption equilibrium. At variable sorption times, the film is quickly washed in ethanol. Then it is extracted for 24 h at room temperature with 500 μL hexane containing as an internal standard 100 mg/L tetradecane.

The extract analysis is made by GC/FID.

The diffusion coefficient is calculated from the sorption kinetics using the square root of time (mass transfer is discarded). The diffusion coefficient is calculated from eq. (6) containing slope B at the origin:

$$D_{\infty} = \pi B^2 e^2 / 16 \quad (6)$$

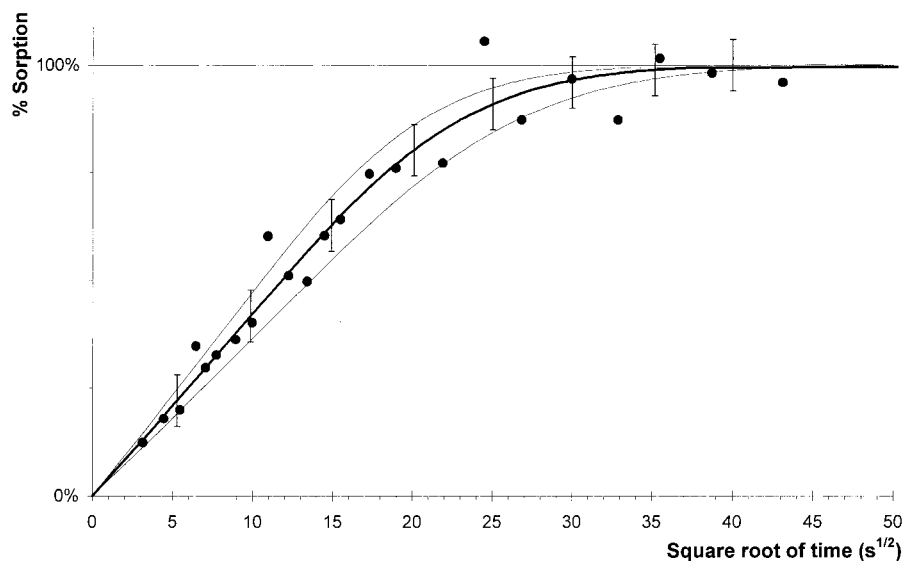


Figure 2 Sorption kinetic of pentadecane in HDPE (67 μm) totally swollen with glyceryl tripelargonate. (●) Experimental values; (—) extreme calculated curves; and (---) theoretic kinetic calculated with $D = 1.6 \times 10^{-8} \text{ cm}^2/\text{s}$.

where D_∞ is the diffusion coefficient in the swollen polymer and e is the thickness of the sample.

As an example of D calculation, sorption kinetics of pentadecane in swollen polypropylene is shown in Figure 2. To all the dots correspond different experiments (different samples). Reproducibility is therefore considered in the experiment. The experimental error is evaluated calculating the average deviation between the best fit and the experimental points (0.06 in the example of Fig. 2).

While taking into account this deviation it is possible to calculate two extreme values for the diffusion coefficient. Systematically carrying out this calculation allowed us to evaluate the error on D_∞ at $\pm 25\%$.

RESULTS AND DISCUSSION

Diffusion Coefficients in Swollen Polymers

Influence of the Molecule Geometry on Swelling Effects

The results obtained in polypropylene with the whole panel of molecules are given in Table I and in Figure 3. As obtained previously on virgin polypropylene,⁴ the homologous series of linear alkanes present a linearity of $\text{Log}(D_\infty) = f(M)$. Moreover, linear alkanes can be considered as the fastest molecules. The triglycerides behave as lin-

ear alkanes as shown previously on virgin polypropylene.⁴ The qualitative comparison of the $\text{Log}(D) = f(M)$ correlation before and after swelling shows the following:

- Needless to say, diffusion coefficients in the swollen polymer are higher than in the virgin one.
- The position of nonlinear molecules compared to the linear alkane straight line is hierarchically the same before and after swelling.

However, some compounds lead to "anomalous" behavior. This is particularly the case with Irganox PS 800, whose shape suggest fast diffusion by reptation while having a low diffusivity, and Irganox 1330, whose shape is spherical and which diffuses as fast as the linear alkane of same molecular weight.

Influence of Molecular Weight

The swelling effect can be quantitatively expressed by the ratio D_∞/D_0 . The results are shown in Fig. 4. As alkanes have a linear dependence of $\text{Log}(D)$ vs M , the ratio of the linear fits have been used instead of the ratio of experimental data.

The influence of swelling is higher with higher molecular weight compounds. The ratio varies from 1 (no effect of swelling with low molecular

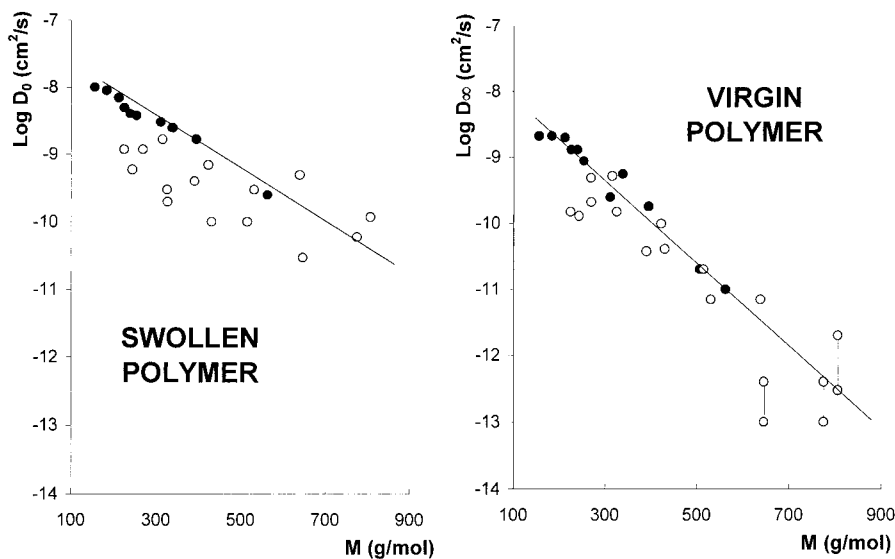


Figure 3 Diffusion coefficients of all the molecules of the panel in virgin (D_0) and swollen (D_∞) polypropylene at 40°C. (●) Linear alkanes; (○) other molecules.

weight compounds) to 100 when the molecular weight exceeds 800 g/mol.

The exponential increase is directly due to the difference of the slopes of the straight lines before and after swelling: after swelling the diffusion coefficient depends less on the molecular weight.

When the molecular weight is below 500 g/mol, the D_∞/D_0 ratio varies from 1 to 20. The Piringer's hypothesis¹⁰ that swelling has no effect on substances whose molecular weight is lower than

that of the swelling agent is perhaps an oversimplification.

Influence of D_0

In Figure 4 the position of triglycerides, which is close to the linear alkanes, confirms that their behavior is close. On the contrary, spherical molecules (Irganox 1330, Irganox 168) have higher ratios than linear alkanes. A first interpretation

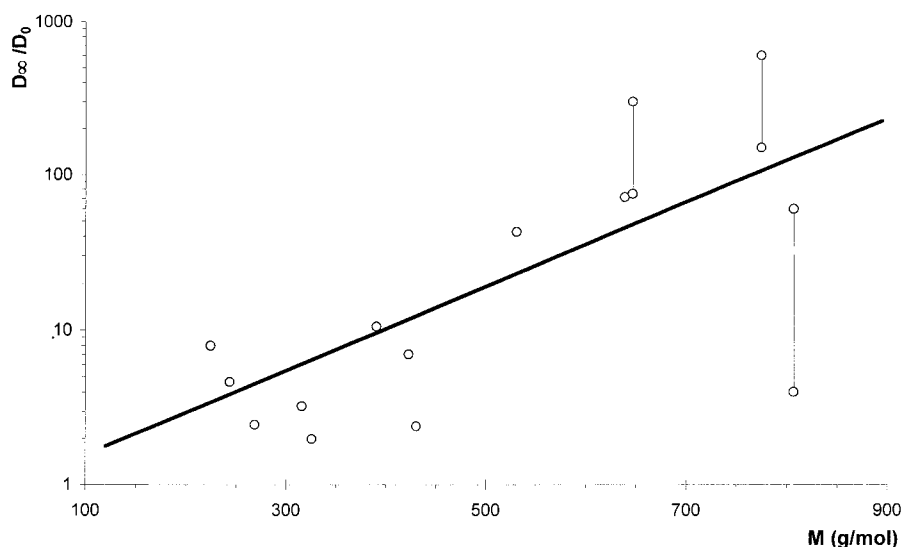


Figure 4 D_∞/D_0 vs M in polypropylene at 40°C. D_0 : virgin polymer; D_∞ : polymer totally swollen with glyceryl tripelargonate. (—) Linear alkanes; (○) other molecules.

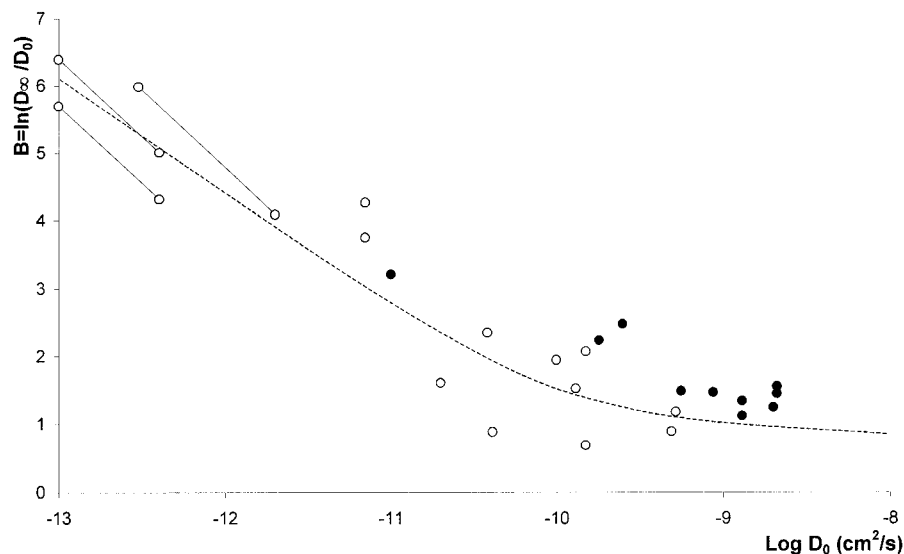


Figure 5 Correlation of swelling factor B vs $\text{Log } D_0$ for all the molecules of the panel in polypropylene at 40°C . (●) Linear alkanes; (○) other molecules.

is that spherical molecules are more sensitive to swelling than linear molecules.

In fact, Figure 5 shows that the swelling factor B (defined by $B = \ln(D_\infty/D_0)$; Ref. 1) is better correlated to D_0 than to molecular weight. If M is replaced by D_0 , there is less scattering in the correlation because of the geometry effect suppression. Indeed, the lower D_0 , the higher the B . The lower is the mobility in the virgin polymer, the higher is the swelling effect.

Similar results have been obtained with linear alkanes on three polyethylene (HDPE, LDPE, LLDPE). They are shown in Table II.

In virgin polyethylene because of specific interactions with the matrix,³ linear alkanes can not be considered as the fastest molecules (as it is the case for polypropylene). But as shown above, the swelling effect can be observed from a $B = f(D_0)$ graph. This way, the specificity of alkanes is not relevant. Figure 6 shows all the data obtained with linear alkanes in swollen polyolefins. A sensitive difference is observed between (PP and HDPE) and (LDPE and LLDPE). The polymers that induce lower diffusion coefficients lead to higher B values (hence higher sensitivity to swelling).

Table II Diffusion Coefficients of Studied Molecules in Virgin and Totally Swollen Polyethylene at 40°C

	HDPE		LLDPE		LDPE	
	D_0	D_∞	D_0	D_∞	D_0	D_∞
Undecane	1.0×10^{-8} a	2.5×10^{-8}	1.9×10^{-8} a	1.7×10^{-8}	1.7×10^{-8} a	1.0×10^{-8}
Tridecane	8.5×10^{-9} a	2.0×10^{-8}	1.8×10^{-8} a	1.1×10^{-8}	1.6×10^{-8} a	9.0×10^{-9}
Pentadecane	7.8×10^{-9} a	1.6×10^{-8}	1.1×10^{-8} a	8.0×10^{-9}	1.3×10^{-8} a	7.5×10^{-9}
Hexadecane	6.4×10^{-9} a	9.0×10^{-9}	1.2×10^{-8}	7.5×10^{-9}	1.0×10^{-8}	5.0×10^{-9}
Heptadecane	5.9×10^{-9} a	8.0×10^{-9}	8.3×10^{-9}	6.5×10^{-9}	9.6×10^{-9}	5.0×10^{-9}
Octadecane	2.2×10^{-9} a	7.0×10^{-9}	4.0×10^{-9} a	5.0×10^{-9}	6.0×10^{-9} a	4.5×10^{-9}
Docosane	4.2×10^{-10} a	5.0×10^{-9}	9.6×10^{-10} a	2.5×10^{-9}	1.4×10^{-9} a	3.0×10^{-9}
Tetracosane	5.3×10^{-10} a	3.5×10^{-9}	6.7×10^{-10}	1.5×10^{-9}	9.9×10^{-10}	2.0×10^{-9}
Octacosane			1.4×10^{-10} a	7.0×10^{-10}	2.5×10^{-10} a	9.0×10^{-10}

^a Studied in previous paper.³

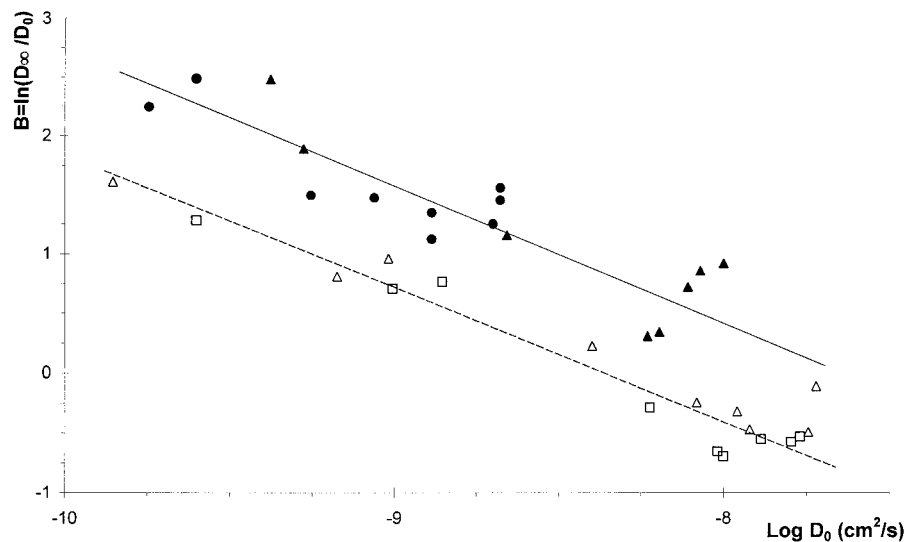


Figure 6 Correlation of swelling factor B vs $\text{Log } D_0$ for linear alkanes in four polyolefins at 40°C . (●) PP, (▲) HDPE, (△) LLDPE, (□) LDPE, (—) master curve for PP and HDPE, and (---) master curve for LLDPE and LDPE.

Temperature Effect

Diffusion coefficients of the molecules were measured in virgin polypropylene at 70°C . Results can be found in Table I and Figure 7. As observed for the swelling effect, temperature does not change the general hierarchy between the molecules (linear molecules faster than spherical molecules). As noticed for swelling, mobility increase leads to a lower diffusivity sensitivity to the mo-

lecular weight: the slope of the alkanes straight line is lower at 70 than at 40°C . This is better illustrated by Figure 8, which shows varying activation energy (E_a) between 40 and 70°C in relation to D_0 . The E_a values are calculated between only two temperatures in a small temperature range (between 40 and 70°C). It is usually not rigorous to calculate from two points one *isolated* E_a ; but here E_a variation is plotted against D_0 ,

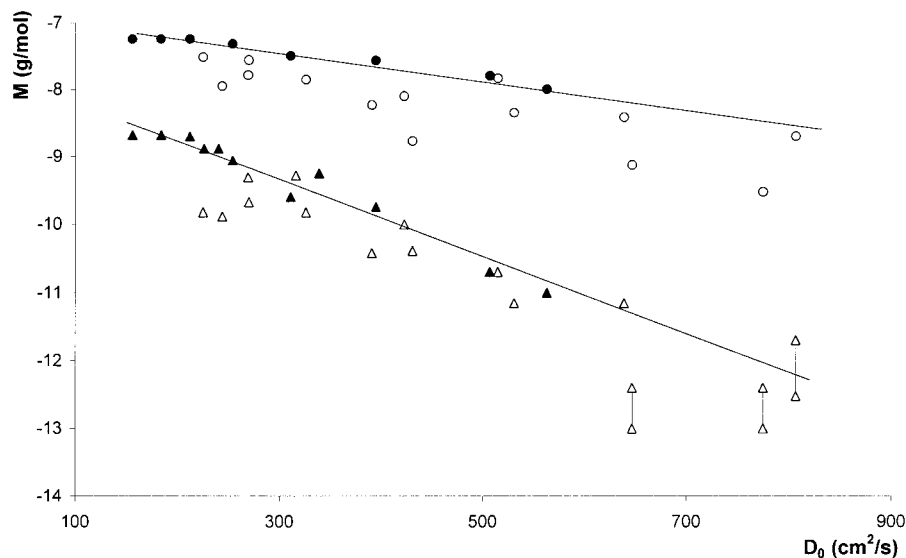


Figure 7 Diffusion coefficients of all the molecules of the panel in virgin PP. (▲) Linear alkanes; (△) other molecules at 40°C . (●) Linear alkanes; (○) other molecules at 70°C .

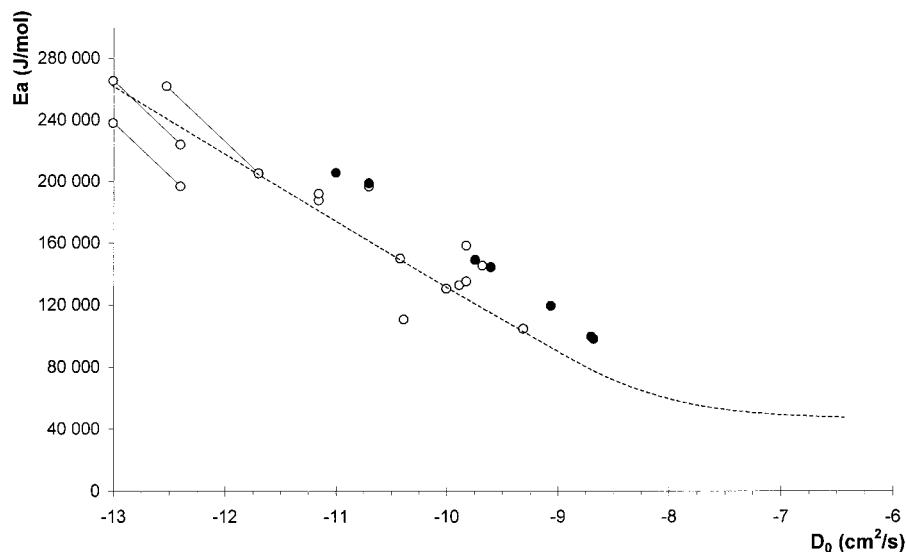


Figure 8 Correlation of activation energy E_a vs $\text{Log } D_0$ for all the molecules of the panel in polypropylene at 40°C. (●) Linear alkanes; (○) other molecules.

leading to a *master curve*. This shows (1) that the method of E_a calculation is acceptable and (2) that activation energy is a directly decreasing function of D_0 .

That E_a is quasi-constant for a given D_0 between 40 and 70°C suggests that E_a principally depends on the increase of mobility of the matrix (temperature does not directly act on the molecule).

However, E_a depends on the geometry of the molecule: $E_a = f(D_0)$ and $D_0 = f(\text{geometry})$. But this is not an argument for the “molecule effect” theory. Indeed, the geometry of the molecule can be interpreted as the “picture” of a free volume geometry, or the picture of the necessary relaxation amplitude for the molecule displacement.

A more precise evaluation shows that alkanes have higher activation energy for the same D_0 .

This means that activation energy is not strictly constant for a given D_0 . A slight effect of the diffusion mode is relevant.

It is important to underline that actually the most used model for diffusion coefficient prediction is the Piringer model,² which considers a *constant* activation energy. As shown in Figure 8, the 100 kJ energy (used by Piringer in polypropylene) corresponds to diffusion coefficients between 10^{-9} and 10^{-8} . The Piringer model is also valid for *low* molecular weight compounds.

The direct calculation of activation energy with 2 points (40 and 70°C) implies that E_a is constant between the two temperatures. However, the in-

crease of activation energy related to the molecular weight leads to illogical values if the temperature is increased above 100°C: the extrapolation above 100°C should express to an increasing $\text{Log}(D) = f(M)$ correlation. It is also not possible to extrapolate the results at higher temperatures. Probably at high temperatures the effect of molecular weight becomes insignificant but there are no possible positive effects. This implies that for a given D_0 , E_a should be a decreasing function of temperature.

CONCLUSION

The same type of correlations were obtained between E_a in relation to D_0 (temperature effect), and B in relation to D_0 (swelling effect). A linear decrease is obtained for the two factors. A horizontal asymptote is observed for B (which tends to zero for very low diffusion coefficients or very low molecular weights). The same limit is predicted for E_a . Thus, the relations are very close, suggesting that phenomena are similar. The lower is the mobility at low temperature in pure virgin polymer, the higher is the temperature or the swelling effect.

Temperature or swelling mainly effect *polymer* mobility. In this case, the *molecule* geometry dependence is only one picture of the real influencing factors: the geometry of free volumes or the

amplitude of polymer local relaxation and their distribution.

Swelling has a temperature like effect. This also means that no specific interactions between simulants and migrant have to be taken into account (for swelling corresponds only to an increase of matrix mobility).

Finally, models for prediction of diffusion coefficients should include

- a correlation for estimation or overestimation of D_0 [for example, by $D_0 = f(M)$ correlation as it is proposed by Piringer];
- $E_a = f[\text{Log}(D_0)]$ and $B = f[\text{Log}(D_0)]$ correlation to extrapolate diffusion properties for high temperatures and for polymer in contact with swelling food simulants.

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