Diffusion Coefficients of Additives in Polymers. I. Correlation with Geometric Parameters

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ABSTRACT: Diffusion coefficients of a broad range of molecules with molecular weight ranging from 100 to 800 g/mol have been measured in polypropylene, by solid/solid contact methods (without liquid contact), at 40°C. The behaviors of the different molecules are compared to those of linear alkanes. The diffusion coefficients are correlated to parameters describing size, shape, and flexibility of the molecules. The concept of weighted fractionated volume is introduced using molecular modeling. It enables the classification of the molecules according to modes of molecule displacement (crawling, jumps, or dual mode). © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2422–2433, 2001

Key words: diffusion coefficient; volume; additive; shape factor; weighted fractionated volume

INTRODUCTION

If prediction of the diffusion coefficient D of an organic molecule in a polymer could be achieved, it would be a very useful tool in areas like food, drug, and cosmetics packaging, and textiles. Several correlations have been proposed, mainly empirical, between the Log of D and the molecular size. They emphasize the importance of molecular size, but do not allow a precise understanding of the influence of changes in molecular structure. From correlation in homologous series, it has been recognized a long time ago that the larger the size of the organic molecule, the lower its diffusion coefficient. In these homologous series, the molecular size can be expressed by the molecular weight,[1–3] the van der Waals volume, the "diameter of the molecule" (calculated from the molar volume, assimilating the molecule to a sphere),[4] or the length of the molecule.[5] However, the size parameters do not describe phenomena that have also been shown to influence the displacement of a molecule in a polymer: its minimum cross section,[6] its shape,[7–9] its interaction with the polymeric matrix,[9] its flexibility.[10] Such changes in the backbone cause deviations from the correlations by several orders of magnitude. It is only estimated that for a given molecular weight, linear molecules would diffuse faster than others, spherical molecules being the slowest.

Recently a compilation of hundreds of published values of D including the molecular weight was made.[11] It shows a large scatter of values. The conclusion was that it was only possible to define an upper value of the diffusion coefficient D for a given molecular weight of the diffusing molecule. Such an upper value of D could be useful to estimate the worst case diffusion of additives from packaging to food. However, the authors concluded that the scatter could at least in part be attributed to the large number of different experimental procedures used. Many data are based on diffusion into a solvent, but this solvent may interact with the polymer, and influence the result. Furthermore, it should be noted that there are only few, if any, data available with high molecular weight compounds. Obviously high molecular weight compounds could have a strong influ-

ence on these Log $D = f(M)$ correlations. In a preliminary study we undertook,[12] we have concluded that these data were the most difficult to obtain, as they require very long experiments and specific experimental procedures.

Since we are involved in a program on food safety related to migration of additives from packaging, we decided to undertake a study that could fill these gaps. We therefore decided to measure diffusion coefficients of additives and of molecules selected on the basis of their molecular structure and functional groups, including compounds up to molecular weight 800 g/mole. Our studies are conducted without any solvent in order to improve the consistency of the results.

A rationalization of the results was then undertaken, taking into account possible mechanisms of displacement of molecules in polymeric networks.

MATERIALS AND METHODS

Diffusing Substances

Molecules of molecular weight ranging from 500 to 807 are added (cf. Table I) to the previously studied set[12]; these molecules were chosen to display a broad variety of chemical structures:

- different molecular weights,
- linear/nonlinear alkanes,
- flexible/rigid molecules, and
- polar/nonpolar molecules.

Common polymer additives are also added to the set.

Polymer

Polypropylene (PP) (supplied by CERDATO France/ELTEX PHV001PF) was tested for diffusion properties. The melting point was determined by differential scanning calorimetry (DSC) (TA Instruments 2920) using onset point of endothermic peak.

PP films: 54 μm thick, $Tm = 138°C$ (onset)

This polymer contains a very low amount of additives which does not interfere with diffusing substances.

Measuring Diffusion Coefficients

An original test (*trilayer test*) was defined to measure very low diffusion coefficients.

A virgin film is pressed at 40°C between two films of the same thickness containing the tested additive. If the concentration in the two lateral films is lower than the solubility at testing temperature, the equilibrium quantity in inner layer equals 1/3 of the total quantity (in the three films). So it is not necessary to run the kinetics until equilibrium. The diffusion coefficient is obtained by fitting the experimental curve (relative quantity of the inner film versus contact time) with a Fick's law resolution program: we assume there an instantaneous mass transfer at interfaces, constant diffusion coefficient, and homogeneous additive repartition in lateral films.

To determine the relative concentration in the inner layer each films of the trilayer stack is dichloromethane extracted and quantified by gas chromatography/flame ionization detector (GC/FID).

In order to obtain suitable concentration films (homogeneous and lower than solubility concentration), the following procedure is chosen: films are immersed for 5 days at 40°C in a saturated solution of the diffusing molecule in hexane. Hexane is desorbed in a ventilated oven for 1 day at 80°C. The previous experiments lead to concentrations in the films that were too high: blooming occurs after annealing at 80°C. Films are then washed with ethanol (a nonswelling solvent), and placed under argon at 100°C for 5 days between two virgin films. These last two films are used in the diffusion test.

The trilayer test was designed to determine very low diffusion coefficients, without having to wait for equilibrium, as the plateau value can be predicted [Fig. 1(a)]. However, for some samples reaching the plateau, the quantity at equilibrium in the inner film was not equal to the theoretical 1/3 of the total quantity [Fig. 1(b)]. Although precautionary measures were taken, the procedure of additive filling in external films (cf. above) leads to a concentration higher than the solubility at 40°C (certainly because the solubility at 100°C is in some cases much higher than the solubility at 40°C). If the plateau is known, the diffusion coefficient is calculated considering its experimental value.

But when the experiment is not conducted to the plateau [Fig. 1(c)], it may not be correct to extrapolate to 33%. An error bar on the diffusion coefficient
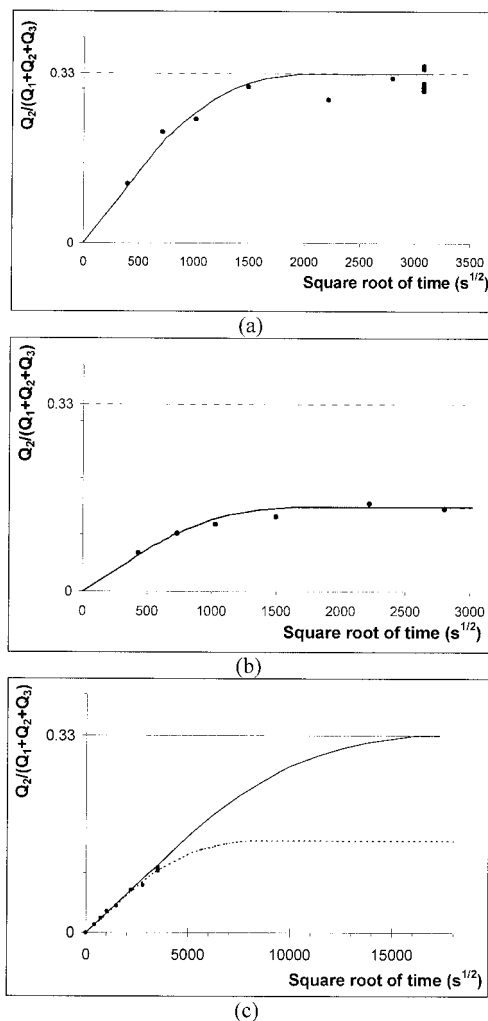
Figure 1 Example of calculation of diffusion coefficients with trilayer test. (a) Irganox 1076: (●) experimental values; (—) calculated curves with $D = 7 \times 10^{-12}$ cm²/s. (b) Tetracontane: (●) experimental values; (—) calculated curves with $D = 1 \times 10^{-11}$ cm²/s. (c) Irganox 1330: (●) experimental values; (—) calculated curves with $D = 1 \times 10^{-13}$ cm²/s; (–) calculated curves with $D = 4 \times 10^{-13}$ cm²/s.

is obtained considering that the real plateau is included between the lowest extrapolable plateau (leading to the highest possible value of D), and the maximum concentration possible (33%, leading to the lowest possible value of D).

The data used in this work are partially issued from previous publication of authors.[12] In this paper, diffusion coefficients were obtained using the "stack method": D is calculated using the fit of diffusion profile in the thickness of a stack of films. The method is precise, experimental variations on D are below a factor two. An example of fitted concentration profile is given Figure 2.

Analytical Determination

Additive concentrations in polymer films in trilayer tests are gas chromatography (FID) determined: the film is extracted by immersion in dichloromethane (1 day at 40°C), and this extract is analyzed by GC.

Injector: On-column (2 μL) $T = 40$°C
Detector: FID $T = 400$°C
Column: DB5-HT (J&W Scientifics) 15 m—0.32 mm i.d.–0.1 μm
Vector Gas: He at 2 mL/min
Temperature program:
  Injection at 40°C
  Isothermal temperature: 2 min
  Ramp at 15°C/min
  Until 400°C

Calculation of Whole Molecule Volume

Optimization of the Molecule Conformation

The conformation searches were performed using Macromodel (Macromodel 6—Colombia University) in a stochastic investigation. Most of the structures were minimized with the MM3 force field, except for Tinuvin P: AMBER was used to handle the N–N–N containing cycle. The most stable conformation of each molecule studied was chosen as a reference for volume calculations, even if in the polymer matrix conformation is at a higher energy state. Moreover, the energy of a molecule during displacement must be higher.

A program was created for the determination of the smallest parallelepiped volume, which contains all the atoms of a molecule or of a molecule fragment.

The following steps are taken:

- There is a 90° rotation by steps of 1° around x axis: to determine the orientation leading to the lowest rectangle surface by projection on yz plane. This orientation is kept for the following steps.
- Same procedure as before for y axis (projection on xz).
- Same procedure as before for z axis (projection on xy).
- Calculation of the parallelepiped volume.
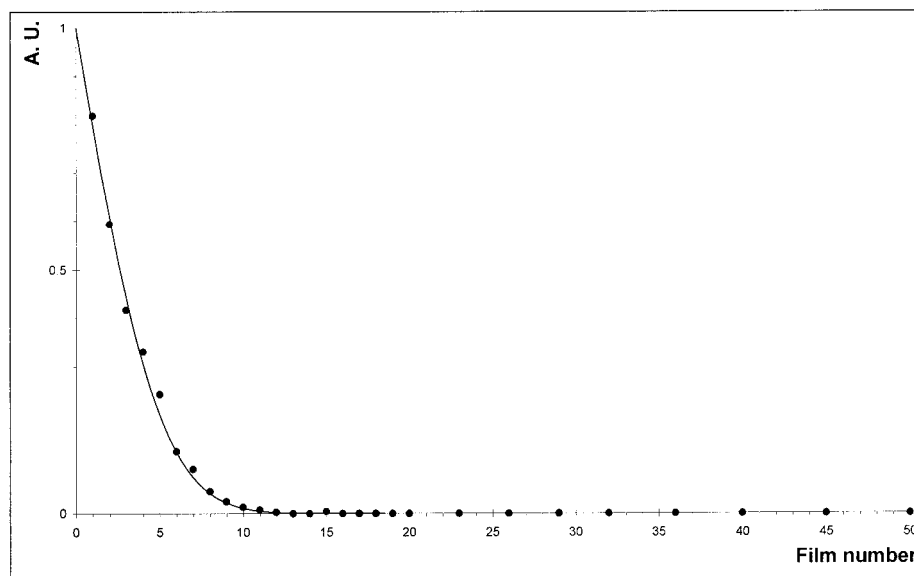- These four steps are repeated until the constant volume of the parallelepiped is obtained ($< 0.1\%$).

Figure 2 Diffusion profile of squalane after 26 days of contact at 40°C with a polypropylene stack (50 films of 54 μm). (●) Experimental values; (—) theoretical profile calculated with $D = 9.9 \times 10^{-11}$ cm^2/s.

In all steps of the calculation, the real dimensions of the atoms are considered (atoms are not represented as points, but as spheres; the dimension of the van der Waals radius is used).

Examples

Four examples of whole volume determination are given Figure 3.

RESULTS AND DISCUSSION

Previous data[12] together with the results of the present study are given in Table I.

Behaviour Groups

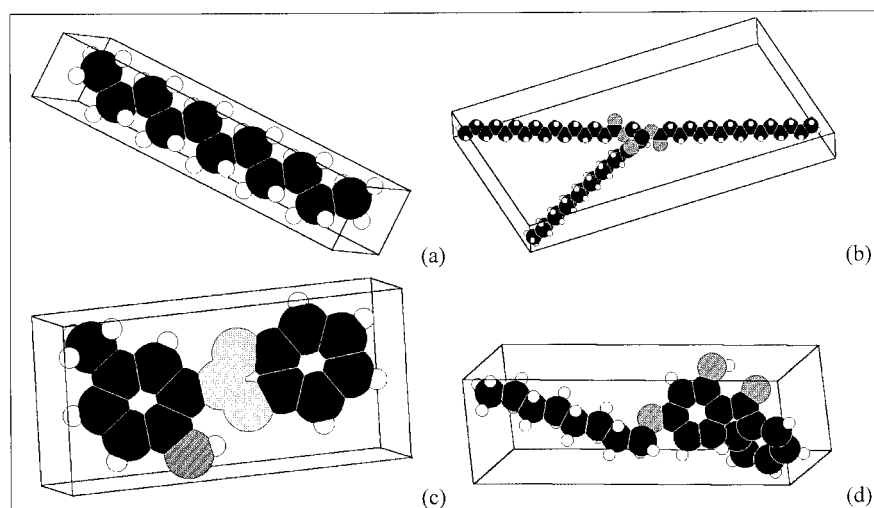When considering the experimental errors, the diffusion coefficients of linear alkanes can be

Figure 3 Examples of whole volume calculations. (A) Undecane, (b) tripalmitin, (c) tinuvin P, and (d) Chimasorb 81.

Table I   Diffusion Coefficients of Studied Molecules at 40°C in Polypropylene

Linear Alkans		Other Molecules		Commercial Additives	
Undecane	2.1×10^{-9} [a]	Triphenyl methane	1.3×10^{-10} [a]	Tinuvin P	1.5×10^{-10} [a]
Tridecane	2.1×10^{-9} [a]	Tetramethyl pentadecane	4.9×10^{-10} [a]	Chimasorb 81	1.5×10^{-10}
Pentadecane	2.0×10^{-9} [a]	Octadecanol	2.1×10^{-10} [a]	DEHP	3.8×10^{-11} [a]
Hexadecane	1.3×10^{-9} [a]	Heptadecyl benzene	5.2×10^{-10} [a]	Uvitex OB	4.1×10^{-11} [a]
Heptadecane	1.3×10^{-9} [a]	Docosanol		Irganox PS800	2.0×10^{-11}
Octadecane	8.7×10^{-10} [a]	Squalane	9.9×10^{-11} [a]	Irganox 1076	7.0×10^{-12}
Docosane	2.5×10^{-10} [a]	Trilaurin	7.0×10^{-12}	Irgafos 168	from 1×10^{-13} to 4×10^{-13}
Tetracosane	5.6×10^{-10} [a]	Tripalmitin	from 3×10^{-13} to 2×10^{-12}	Irganox 1330	from 1×10^{-13} to 4×10^{-13}
Octacosane	1.8×10^{-10} [a]				
Hexatriacontane	2.0×10^{-11}				
Tetracontane	1.0×10^{-11}				

[a] Studied in previous paper.

bracketed between the two straight lines of Figure 4. This area can be taken as a reference for the classification of the different molecules, according to their Log(D) and the differences of shape and mobility.

Three different families are thus defined: (1) diffusion behavior is the same as that of linear alkanes with the same molecular weight, (2) diffusion behavior is lower than that of linear alkanes with the same molecular weight, and (3) intermediate behaviors.

1. The behavior of molecules 1, 3—5, 7, and 12 (Fig. 4) are close to linear alkanes: All these molecules have long alkyl chains and no bulky groups. Only heptadecyl benzene has an aromatic group, but the backbone is not substituted. All these molecules have a high mobility and flexibility, and their structure suggests a crawling diffusion mode, as it is supposed to be the case for linear alkanes. It is also logical to obtain diffusion coefficients close to that of the linear alkanes which have the same molecular weight.

2. Molecules 8, 9, 11, and 13–15 (Fig. 4) have totally different geometric characteristics: Their shape tends to be spherical, because of

   - several aromatic groups (molecules 11, 13, 15) or chain branchings on small chains (molecule 9);
   - rigid heterocycles (molecules 8, 14).

These molecules are supposed to diffuse by jumps (from a free volume to another). This diffusion mode implies an instantaneous displacement of the molecule in its totality (this is not the case for the crawling mode of molecules having many degrees of freedom). These diffusion coefficients of these compounds are lower than those of linear alkanes. The diffusion rate of UVITEX[14] should be predicted to be specially low. However, this molecule is close to alkanes, and that is doubtless related to its low cross section (planar molecule).

3. Molecules 2, 6, and 10 (Fig. 4) lead to intermediate behavior: Two different cases can be observed:

   - Some of these molecules (2 and 10) have both flexible groups and rigid parts. It is not possible to decide whether only one or two mechanisms of displacement occur at the same time in the same molecule. These molecules diffuse by jumps but a part of the molecule can relax during their displacement, as it is the case for crawling. This presentation of the diffusion suggests a dual mode
   - The diffusion coefficient of a primary linear alcohol is lower than that of the linear alkane of the same molecular weight (case of molecule 6). Although the polypropylene is not a polar matrix, the polarity seems to have an effect on diffusivity. A possible interpretation is the formation of dimers in
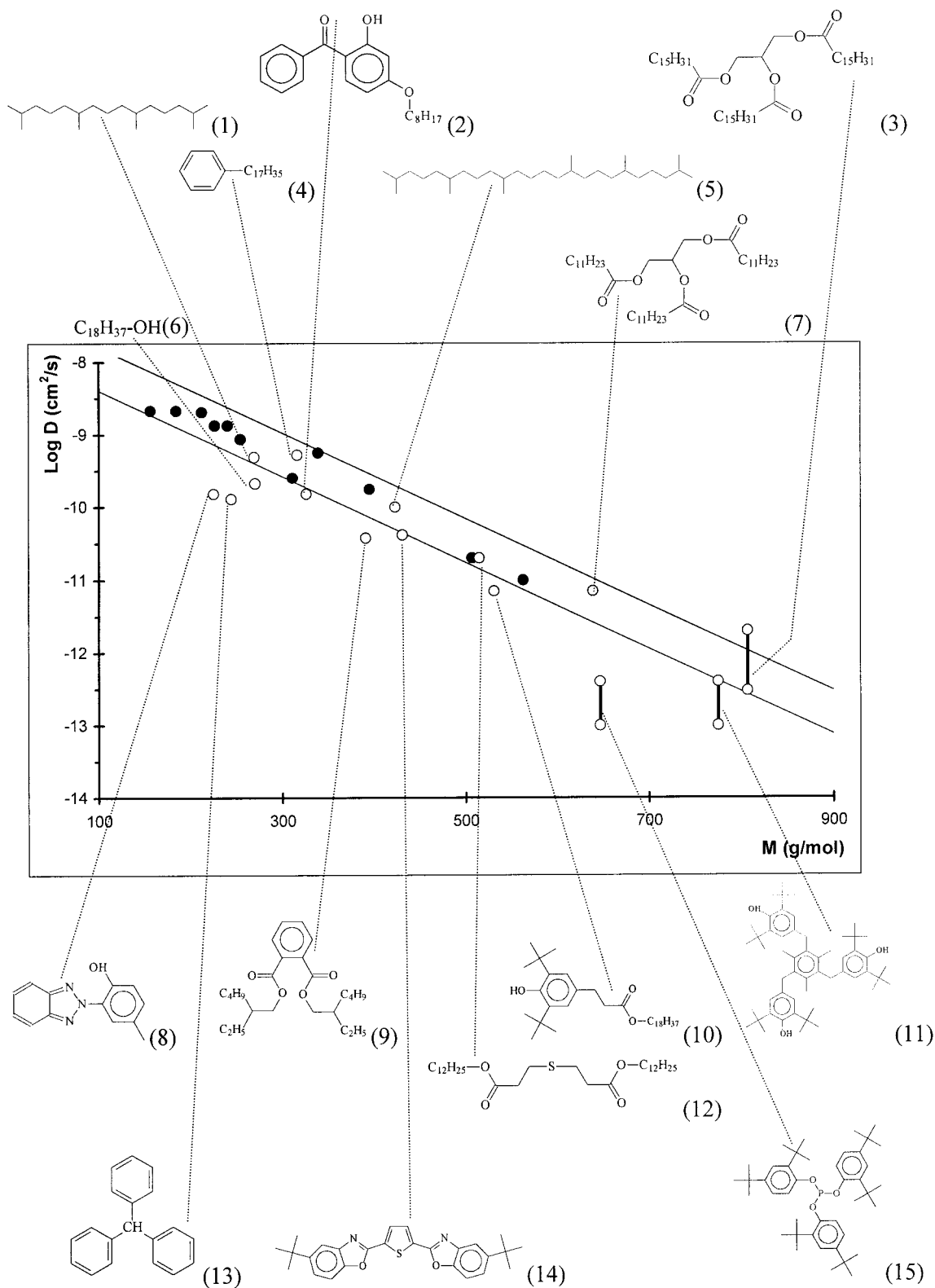
Figure 4   Correlation Log $D = f(M)$ in polyproylene at 40°C. (●) Linear alkanes; (○) other molecules (with formula).

Table II   Whole Volumes of Molecules (in Å³)

Linear Alkans		Other Molecules	
C11	120	Triphenyl methane	444
C13	140	Tetramethyl pentadecane	646
C15	159	Heptadecylbenzene	404
C16	169	Squalane	1440
C17	179	Octadecanol	198
C18	189	Trilaurin	3040
C22	229	Tripalmitin	5380
C24	249	Tinuvin P	193
C28	289	Chimasorb 81	802
C36	368	DEHP	880
C40	408	Uvitex OB	551
		Irganox PS 800	554
		Irganox 1076	1638
		Irgafos 168	1962
		Irganox 1330	1983

the material by hydrogen bonding between two alcohol molecules.

The correlation between diffusion coefficients and molecular weight of the migrant allows to verify a linear dependence of $\text{Log}(D) = f(M)$ in a homologous series of molecules. Except for the case of linear alcohols, the gap between any molecule and a linear molecule of the same molecular weight is only connected to its geometry.
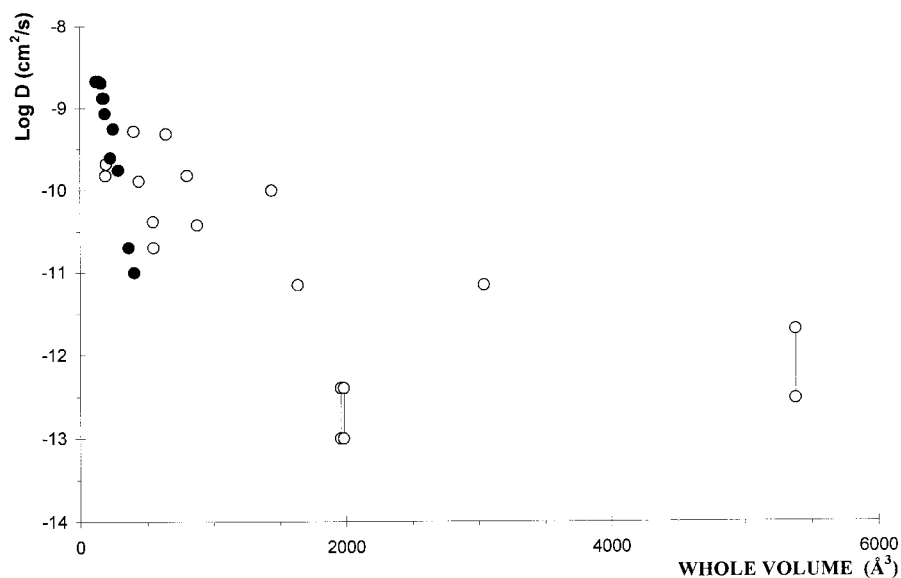
Whole Volume of Molecules

The volume of the molecule has to be considered first. As discussed previously, the van der Waals volume should give the same results as the molecular weight since they are proportional. But van der Waals volume is sometimes much lower than the real volume occupied by the molecule. Our choice was to determine the whole volume of the molecules using the following systematic procedure:

- The molecule conformation used is the stablest conformation of the molecule calculated using MACROMODEL.
- The whole volume is defined by the lowest volume parallelepiped containing the molecule in the above conformation.

Whole volumes (V) are given in Table II and the correlation with $\text{Log}(D)$ is shown (Fig. 5). The dispersion is very high. Compared to the volume of linear alkanes, the whole volumes of other compounds are largely overestimated. The following conclusions are drawn:

- The choice of studying the molecules in their most stable conformation is not representative of reality. In this conformation, the molecule tends to occupy the maximum volume in order to minimize repulsion between at-
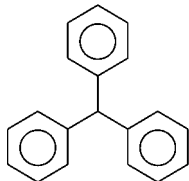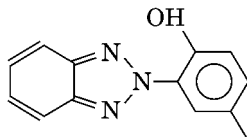

Figure 5   Correlation $\text{Log } D = f$(Whole volume) in polypropylene at 40°C. (●) Linear alkanes; (○) other molecules.

Table III   Fractionated Volume Calculations

Molecule	Fragment	Dimensions of the Box (Å)	Fractionated Volume (Å^3)
Linear alkans	C_nH_{2n+2}[a]	$2.60 \times 2.99 \times L$	$7.774 \times L$
Triphenyl methane	[b]	$4.96 \times 9.04 \times 9.91$	444
Tetramethyl pentadecane	$C_{15}H_{32}$[a] $4 \times CH_4$	$2.60 \times 2.99 \times 20.51$ $2.04 \times 2.04 \times 2.04$	193
Heptadecylbenzene	$C_{17}H_{36}$[a]	$2.60 \times 2.99 \times 23.07$ $1.93 \times 5.06 \times 5.72$	235
Squalane	$C_{24}H_{50}$[a] $6 \times CH_4$	$2.60 \times 2.99 \times 32.02$ $2.04 \times 2.04 \times 2.04$	300
Octadecanol	$C_{18}H_{37}OH$[a]	$2.62 \times 2.99 \times 25.34$	199
Trilaurin	$3 \times C_{11}H_{23}—COO—CH_3$[a]	$2.62 \times 3.90 \times 18.68$	573
Tripalmitin	$3 \times C_{15}H_{31}—COO—CH_3$[a]	$2.64 \times 3.94 \times 23.78$	742
Tinuvin P	[b]	$2.41 \times 6.80 \times 11.83$	194
Chimasorb 81	C_8H_{18}[a] [b]	$2.60 \times 2.99 \times 11.57$ $3.70 \times 6.13 \times 10.84$	336
DEHP	$2 \times$ [b]	$3.59 \times 6.53 \times 10.92$ $1.93 \times 5.06 \times 5.72$	568
Uvitex OB	[b]	$4.95 \times 5.12 \times 21.75$	551
Irganox PS 800[c]	$2 \times C_2H_5—COO—C_{12}H_{25}$[a] S	$2.61 \times 4.11 \times 21.20$ $2.62 \times 2.62 \times 2.62$	473
Irganox 1076	$C_2H_5—COO—C_{18}H_{37}$[a] [b]	$2.71 \times 4.14 \times 28.87$ $4.96 \times 5.88 \times 10.28$	624

Table III *Continued*

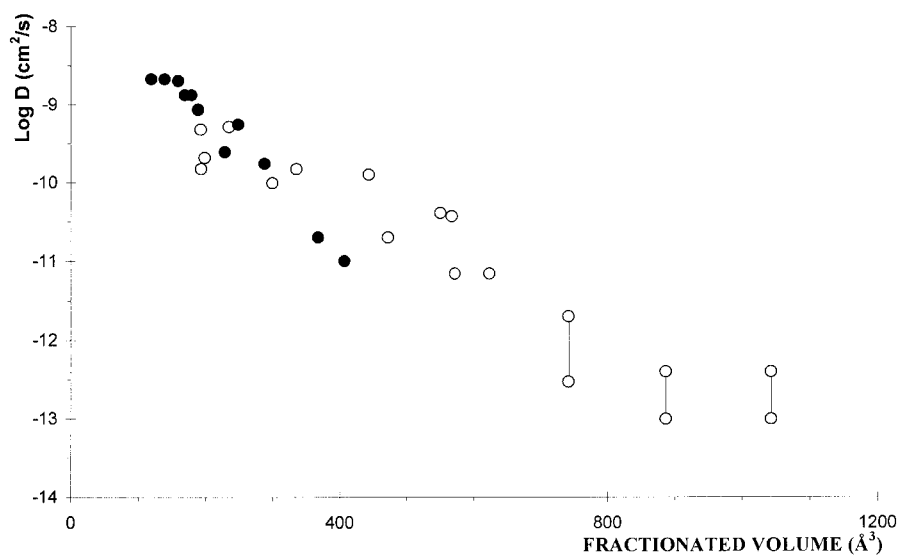| Molecule	Fragmentation		Fractionated Volume (Å³)
	Fragment	Dimensions of the Box (Å)	
Irgafos 168	PO₃	$3.05 \times 3.95 \times 4.27$	887
		$4.59 \times 7.29 \times 8.32$	
	$3 \times$ [structure] b		
Irganox 1330	[structure] b	$2.55 \times 7.25 \times 7.79$	1043
	$3 \times$ HO—[structure] b	$4.96 \times 5.88 \times 10.28$	

ª Linear conformation.
ᵇ Stable conformation.
ᶜ Fractionation linked to the impossibility to have a linear conformation with the S atom.

Figure 6   Correlation Log $D = f$(Fractionated volume) in polypropylene at 40°C. (●) Linear alkanes; (○) other molecules.

oms. In a polymer matrix, diffusion mechanisms imply conformations characterized by a higher energy. But it is difficult to give systematic criteria for these molecule deformations.

- Considering the whole molecule volume by insertion of the molecule into a box amounts to overestimating the real volume taken by the molecule for the diffusion. The most realistic picture is certainly intermediate between the van der Waals volume and the whole volume (cf. overestimated box of tripalmitin in Fig. 3).
- The sole volume criterion leads to considering that the diffusion of all the molecules (except linear alkanes) occurs by jumps, while "alkanes like" and intermediate molecules are supposed to diffuse rather by crawling (cf. for example the case of tripalmitin at 5380 Å^3 in Fig. 5).

Thus the proposed fragmentation of the molecule volume by considering separately the mobility of each part of the molecule.

Fractionated Volume

In each molecule, groups of atoms can belong to two different classes:

- Groups with high degrees of freedom: Long and flexible chains that can take several conformations making the displacement easy. These volume parts are also calculated taking into account linear conformations (leading to the lowest possible volume). The box shape of the volume is kept.
- Rigid parts: They are generally constituted by cycles or short chains (for which the conformation is locked). These volume parts are calculated considering steric effects, so using the most stable conformation.

The fractionated volume of the molecule corresponds to the sum of the different partial volumes obtained.

The molecules were fragmented as shown in Table III. The correlation with D is better than that obtained using the whole volume (cf. Fig. 6).

The dispersion increases with the volume of the molecule.

Linear alkanes have the lowest diffusivities for a given fractionated volume. The shape charac-

teristics, and by extension the diffusion mode are left out when using fractionated volume.

Shape Factor

The shape of a molecule has an incidence on the diffusion mode: the probability for a long molecule to have many degrees of freedom is high, and this facilitates molecule displacements by crawling.

There are two ways of approaching the shape of the molecules looking at the following:

- The shape of the whole molecule. This possibility is not in good agreement with the remarks made on the whole volume: the real shape of the whole molecule in a polymer matrix during the diffusion does not correspond to the most stable conformation. This real case cannot be predicted. Moreover there are many different conformations corresponding to the real cases.
- The shape of each parts of the molecule as defined in the previous paragraph. This is an improvement of the fractionated volume approach. This was the approach chosen.

The cube was chosen as the reference volume to describe spherical molecule parts. A shape factor is defined by equation 2, for a part of the molecule:

$$\varphi = \frac{\text{Surface of the parallelepipedic box}}{\text{Surface of the cube of same volume}}$$

$$= \frac{ab + bc + ca}{3(abc)^{2/3}} \quad (2)$$

where a, b, and c are the dimensions of the lowest volume box.

The shape factors of each part of the molecule are calculated. The shape factor of the whole molecule is the average of the shape factors of each part weighted according to the number of atoms (except hydrogen atoms). The results of this calculation are given in table 4.

The shape factor increases from 1 (spherical molecule incorporated into a cube) to 1.8 (the longest molecule of the studied panel: linear C_{40}). Figure 7 shows the values of φ (represented by the diameter of the dots) in a $\text{Log}(D) = f$(fractionated volume) graph. For a given diffusivity, the highest shape factor (linear molecule) corresponds to the lowest fractionated volume.

Table IV   Shape Factors (φ) of Studied Molecules

Linear Alkanes		Other Molecules	
C11	1.29	Irgafos 168	1.03
C13	1.34	Triphenyl methane	1.05
C15	1.39	Irganox 1330	1.07
C16	1.41	DEHP	1.11
C17	1.43	Chimasorb 81	1.13
C18	1.45	Uvitex OB	1.21
C22	1.54	Tinuvin P	1.25
C24	1.57	Irganox 1076	1.31
C28	1.64	Tetramethyl pentadecane	1.31
C36	1.77	Trilaurin	1.33
C40	1.82	Heptadecylbenzene	1.36
		Irganox PS 800	1.36
		Tripalmitin	1.41
		Squalane	1.46
		Octadecanol	1.47

The product of these two parameters ($\varphi \times$ fractionated volume) gives a "weighted fractionated volume" that leads to an acceptable correlation with Log(D) (cf. Fig. 8): most of the dots thus obtained are located in the area defined by linear alkanes.

The molecules having a different behavior are as follows:

- Octadecanol: We have seen that its particular behavior may be connected to the formation of dimers associated by hydrogen bonds.

- Tinuvin P: The correlation proposed considers *indirectly* the effect of the rigidity—both by the shape factor and by the calculation of the volume from molecule groups that can move "independently" from the other parts of the molecule. Such rigid structures (rigid but not spherical) are imperfectly described by this model.

CONCLUSION

Diffusion coefficients of a broad set of molecules in PP at 40°C have been correlated to various molecular parameters: the molecular weight and an efficient diffusion volume. In order to evaluate the influence of the flexibility and of the mode of displacement, the empirical concept of "weighted fractionated volume" was introduced. Even if the correlations are satisfactory, the approach is not designed to provide tools nor equations to predict D from molecular parameters. It rather aims at a better understanding of the mechanism of displacement in polymeric matrixes: two main mechanisms seem to be effective: crawling, based on the large number of degrees of freedom of long alkyl chains, and jumps for rigid molecules. Intermediate behaviors are obtained. They can be described by jump displacements facilitated by the more or less easy relaxation of other parts of the molecule.

Temperature and swelling of the polymer by solvents and foodstuffs are likely to change the
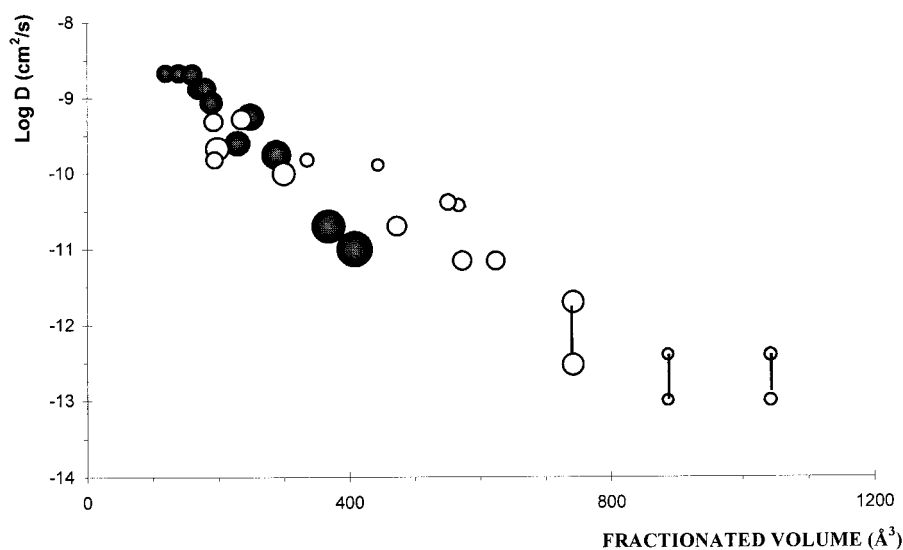

Figure 7   Representation of the shape factor φ (size of point proportional to φ^2) on Log(D) = f(Fractionated volume) correlation. (●) Linear alkanes; (○) other molecules.

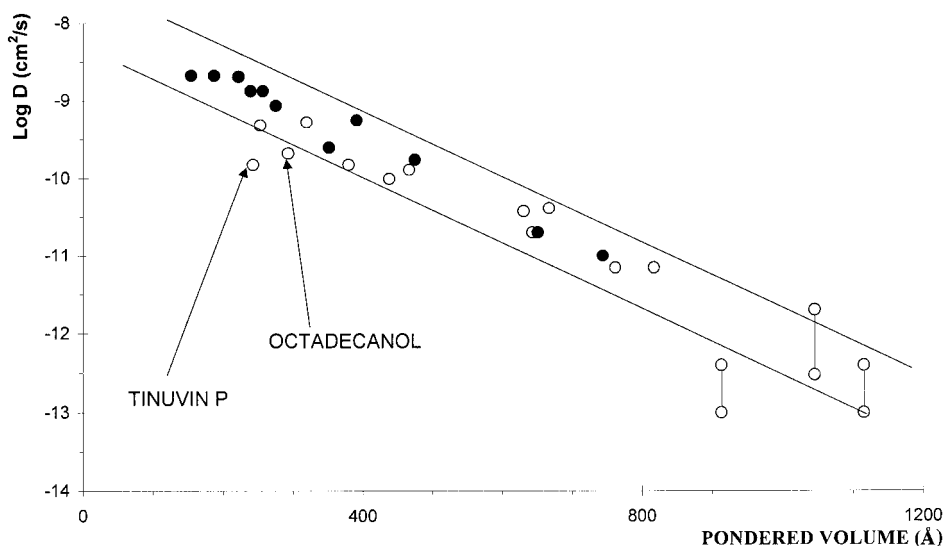**Figure 8**   Correlation Log $D = f$(Pondered volume) in polypropylene at 40°C. (●) Linear alkanes; (○) other molecules.

correlations proposed here. These two factors are studied in Part II of this paper.

REFERENCES

1. Al-Malaika, S.; Goonetileka, M. D. R. J.; Scott, G. Polym Degrad Stability 1991, 32, 231–247.
2. Moisan, J.Y. Eur Polym J 1980, 16, 979–987.
3. Schlotter, N. E.; Furlan, P.Y Polymer 1992, 33, 3323–3342.
4. Berens, A. R.; Hopfenberg, H. B. J Membrane Sci 1982, 10, 283–303.
5. Moisan J.Y. Eur Polym J 1981, 17, 857–864.
6. Aitken, A.; Barrer, R. M. Trans. Faraday Soc 1955, 51, 116–130.
7. Feigenbaum, A.; Riquet, A. M.; Ducruet, V.; Scholler, D. J Chem Educ 1993, 70, 883–886
8. Rogers, C. E. In Physics and Chemistry of the Organic Solid State—Volume II; Fox, D.; Labes, M., Weissberger, A., Eds.; Interscience Publishers: New York, 1965.
9. Scott, G. Food Additives and Contaminants 1988, 5(1), 421–432
10. Saleem, M.; Asfour, A.-F. A.; De Kee, D. J Appl Polym Sci 1989, 37, 617–625.
11. Brandsch, J.; Mercea, P.; Piringer, O. In Piringer, O., Baner, A. Eds.; Plastic Packaging Materials for Food. Barrier Function, Mass Transport, Quality Assurance and Legislation; WILEY—VCH2000, 2000.
12. Reynier, A., Dole, P.; Feigenbaum, A. Food Additives and Contaminants 1999, 16(4), 137–152.