

Overestimated diffusion coefficients
for the prediction of worst case migration from PET:
application to recycled PET and to functional barriers assessment

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SUMMARY

This paper defines parameters which can be used to predict worst case migration from recycled PET bottles, with and without a functional barrier. Starting with a set of diffusion coefficients determined in well defined experimental conditions (temperature, presence or not of a solvent, with and without swelling effect), empirical equations for the diffusion coefficient of a migrant or a pollutant in PET at 40°C are given as a function of its molecular weight. An equation is also derived for migration from PET into water. Surrogates representative of worst case migrants are identified, which is discussed in terms of molecular weight, structure and interaction with the PET matrix. In a second part of the paper, the empirical equations have been used to simulate the migration from monolayer bottles and from multilayer bottles with different geometries of functional barrier, as a function of pollutants molecular weight. Since the diffusion coefficients are overestimated, the calculated migration is also overestimated, which provides a margin of safety. The advantage of the functional barrier technology is compared to direct food contact route, as a function of food contact time. In a last part of the paper, the effect of testing temperature is investigated. Based on a literature survey, the activation energy of pollutants is shown to increase roughly with their molecular weight. A worst case activation energy of 80 kJ/mol is proposed, allowing to extrapolate migration data from a higher temperature (values calculated at 40°C or determined at 60 °C) to room temperature. The possible use of this activation energy to design tests for functional barriers is discussed.

KEY WORDS

PET, Functional barrier, Modelling, Food packaging, Food safety, Safety assessment, Recycling, Surrogates, Migration, Diffusion

INTRODUCTION

Food contamination by migration of low molecular weight species from plastic packaging is controlled by several parameters. Among them, diffusion properties in polymers have focused much attention. An approach to predict migration with a safety margin, using an overestimation approach, has been proposed by Piringer [1, 2], based on overestimated values of diffusion coefficients. A large set of experimental diffusion coefficients is plotted against molecular weight (M), and an empirical equation [$\log D^* = f(M)$] is proposed, where D^* is an overestimated value of all the diffusion coefficients.

This method has been applied successfully to polyolefins and the empirical equation (1) has been obtained on the basis of D values from literature.

$$\log D^* = A M + B/T + C \quad \text{equation (1)}$$

where A, B, C are constants

The experimental conditions as well as the mathematical background strongly differed from one D value to another in this literature compilation. However the very large number of available data gave confidence into equation (1) [1, 2, 3]. In a second step, predicted and

experimental migration values were compared, which allowed a readjustment of the A_p , B and C coefficients.

For other polymers, the problem is to find enough and selected literature data to propose such correlations: “enough” because a large scope of molecular weights, shapes, sizes, geometries, and functionalities must be covered; “selected” because there is a need of diffusion coefficients obtained in well defined experimental conditions (concentration, liquids in contact interacting or not with the polymer). Few data are available for glassy polymers, where experiment duration is much larger, due to lower D values. This is why, in a previous work, we have generated reference data for PET [4], for representative sets of molecules and on the basis of diffusion and specific migration tests [5]. In the present paper, we will use these experimental data to propose empirical equations for overestimated diffusion coefficients in PET at 40°C. The relationships will then be used to predict diffusion/migration behaviour at 40°C, for monolayer bottles and for multilayer (with functional barriers) bottles. Concerning PET bottles with functional barriers, we have shown that diffusion during processing of bottles could be neglected despite the high temperature during co-injection, given mainly the large thickness of preforms [6]. Therefore only the diffusion step during food storage has to be considered in this paper, assuming perfect repartition of migrants in the core of the recycled inner layer.

NUMERICAL SIMULATIONS

The numerical methods and assumptions have been presented in previous papers [7,8]. A freeware is available on the INRA web site (“MULTIWISE”).

GLOSSARY OF THE MAIN PARAMETERS USED

C_{Food}^*	Maximum tolerable concentration of pollutants in food, fixed by law (related to threshold of toxicological or regulatory concern)
$C_{P,0}$	Initial concentration of pollutants in plastic
$C_{P,0}^*$	Maximum tolerable concentration of pollutants in PET articles. It depends on C_{Food}^* and on M
D^*	Worst case diffusion coefficient, determined empirically from a graphical correlation $\log D = f(M)$
$D_{PET/PET}^*$	Worst case diffusion coefficient of surrogates or migrants in PET
$D_{PET/PET,M>130}^*$	Worst case diffusion coefficient of surrogates, migrants or pollutants with $M > 130$ g/mol in PET
$D_{PET/PET,M<130}^*$	Worst case diffusion coefficient of surrogates, migrants or pollutants with $M < 130$ g/mol in PET
$D_{PET/aqu}^*$	Worst case diffusion coefficient of surrogates during migration tests into water
$D_{PET/aqu,M>130}^*$	Worst case diffusion coefficient of surrogates, migrants or pollutants with $M > 130$ g/mol in PET in contact with water (function of M)
$D_{PET/aqu,M<130}^*$	Worst case diffusion coefficient of surrogates, migrants or pollutants with $M < 130$ g/mol in PET in contact with water
$D_{PET/EtOH,M>130}^*$	Worst case diffusion coefficient of surrogates, migrants or pollutants with $M < 130$ g/mol in PET in contact with ethanol (function of M)
$m_{Food,t}$	Mass of pollutant or surrogate transferred from PET into food at time t
M	Molecular weight of the pollutant or of the surrogate
t_{max}^*	Maximum time of use of a package made with recycled plastic, before the contamination of food, calculated with overestimating assumptions, reach C_{Food}^*

Experimental diffusion data have been described in previous papers [4, 5]. Averaged values of D^* at the plateau (values for $M < 130$) and straight line equations correlating $\log D^*$ and M (all values available) are calculated assuming a 90 % confidence level using appropriate Student factors (N=4 S=1.53; N=5 S=1.48; N=8 S=1.4, N=13 S=1.35; N=15 S=1.34). The

overestimated equations are obtained by adding the standard deviation (corrected by the adequate Student factor) to the average values or to the straight line regressions.

RESULTS AND DISCUSSION

In previous papers, we have published sets of experimental diffusion coefficients, measured in consistent conditions, with low concentrations of surrogates in PET, in presence or in absence of simulants. In the present paper, we discuss these data in order to define worst case surrogates, and worst case values of the diffusion coefficients of pollutants. We also propose an approach for testing of multilayer and functional barrier materials.

I. Diffusion coefficients in PET.

In part I of this work we have measured sets of diffusion coefficients of a large panel of surrogates, with and without liquids in contact, and using different sources of oriented PET. Differences between individual sets of values have been discussed [4]. In the present paper, in order to focus on worst case situations, we will take into account only the highest diffusion coefficients obtained previously in virgin PET, in PET plasticized by water and in PET plasticized by ethanol. The “highest” means that when different values of diffusion coefficients could be calculated (depending on the assumptions on the equilibrium state), we selected systematically the largest possible D value for the present work. These worst case values are compiled in table 1.

The largest number of experimental diffusion coefficients were obtained for diffusion in virgin PET (from thin film to thin film, in stacks) and into ethanol (migration from PET mono- and multilayer bottles into ethanol monitored over 18 months). With an aqueous test medium (migration into 3 % acetic acid monitored over 18 months), only the lowest molecular surrogates and those which were soluble in the test medium could be detected, and only a few diffusion coefficients could be determined. The diffusivities of surrogates in virgin PET, into ethanol and into water are displayed in function of their molecular weight in Figure 1. The general trend is that diffusion coefficients decrease when molecular weight increases

[2]. Two zones are observed in figure 1: the lowest molecular weight compounds ($80 < M < 130$ g/mol) (dimethyl sulfoxide, toluene, phenol, 2,4-pentanedione and chlorobenzene, entries 1-5 in table 1) have close diffusion coefficients both in virgin PET and in PET plasticized by ethanol, and a plateau is shown. Log D then strongly decreases with $M > 130$ g/mol.

In literature, higher diffusion coefficients are reported for PET, but they are all for species with a lower molecular weight (mainly gaseous compounds, with $2 < M < 60$ g/mol) than our surrogates (> 80 g/mol). We think that the compounds of our plateau are indeed worst case substances (entries 1-5, table 1), since they all have planar structures (known to diffuse easily through polymeric networks), and since they are representative of different hydrogen bonding abilities which may slow down diffusion in a PET matrix (hydrogen bond acceptor) [9].

2,4-Pentanedione (entry 4) is the fastest diffusing compound of our surrogates, both in neat and in plasticized PET. This can be understood considering that it is mainly under its enolic form, which forms intramolecular hydrogen bonds and therefore does not interact with the PET matrix. The difference with other surrogates is even larger in the presence of water or ethanol, which are both hydrogen bond acceptors and donors (figure 1). This again can be understood by considering that 2,4-pentanedione, although polar and water soluble, remains predominantly under its enolic form, even in aqueous media.

II. Overestimated diffusion coefficients in neat PET and in PET plasticized by ethanol.

To predict migration with a safety margin, one has to define maximum values of D for a given molecular weight. The upper bound D values will be quoted D^* . With the surrogates studied here, we clearly have to distinguish two zones:

For $M > 130$ g/mol, the line with equation (2) represents the worst case

$$\log D_{\text{PET/PET}, M > 130}^* = -0.0289 M - 9.994 \quad \text{equation (2)}$$

For $80 < M < 130$ g/mol, the previous equation would lead to a too severe overestimation and it seems preferable to introduce a plateau corresponding to equation (3). The plateau displayed in figure 1 ($80 < M < 130$ g/mol) corresponds to the 2,4-pentanedione diffusion coefficient.

$$\log D_{\text{PET/PET}, M < 130}^* = - 13.12 \quad \text{equation (3)}$$

Worst case pollutants with $M < 130$ g/mol

In this section we discuss whether the surrogates used in this work, especially those with the lowest molecular weight, really represent worst case situations in terms of diffusion properties (D and D^*).

It may be surprising to define a plateau for all compounds with molecular weight in the range 80 - 130 g/mol. However, we think that this is justified even for any surrogate contaminant with $M < 130$ g/mol. Despite their large diffusion coefficients, as discussed in the previous section, compounds with molecular weight below 80 g/mol are not subject to migration restrictions, unless they are highly toxic: ethylene ($M = 28$ g/mol), propylene ($M = 42$ g/mol) and butene ($M = 56$ g/mol) have no SML in the EU regulation, in contrast with hexene ($M = 80$ g/mol) and higher molecular weight 1-alkenes. The reason is that risk assessors consider that due to their large volatility, compounds with molecular weight below 60 g/mol are readily evaporated from the finished materials or articles (Synoptic, 2003). Of course, compounds like vinyl chloride ($M = 62.5$ g/mol) or ethylene oxide ($M = 44$ g/mol), which are highly toxic, are submitted to restrictions, as minute residual amounts may be a concern for public health. In the specific case of PET, the drying steps for several hours at 150 – 180 °C, which are associated to each process, contribute to the evaporation of the very low molecular weight pollutants. Data on evaporation during PET drying can be found in the previous paper [5].

The assumption that the lowest molecular weight compounds are of minor concern for safety assessment because they are evaporated is also implicit in all publications and guidelines [10, 11, 12], which all recommend surrogates with molecular weight larger than 80 g/mol: trichloroethane, chloroform, toluene, chlorobenzene, phenol, hexanol, dimethyl sulfoxide, pentanedione [5, 11, 13, 14, 15, 16]. Propylene glycol ($M = 64$ g/mol) is the only compound with molecular weight below 80 g/mole we found in these references; however its strong

capacity to form hydrogen bonds with PET strongly reduces its volatility and most likely also its diffusion coefficient.

The molecular shapes of our surrogates with $80 < M < 130$ g/mol are very similar: they are all planar molecules, with little or no degree of freedom, and are therefore among the fastest diffusing chemicals in that molecular weight range [9]. They have very close experimental diffusivities (between $3 \cdot 10^{-14}$ to $7.7 \cdot 10^{-14}$, table 1). For all these reasons, it can be accepted that the surrogates selected here (entries 1-5, table 1) represent worst case pollutants.

Plasticization by ethanol

Actual (D) and overestimated (D*) diffusion coefficients are lower for PET/PET than for PET/Ethanol tests, which is consistent with the strong plasticizing effect of ethanol [4, 5]. The slope for the overestimated [0.0148] is lower with ethanol than without solvent (0.0289) (equation 1). This is also in agreement with general knowledge on swelling and thermal effects described for other polymers [17, 18].

III. Overestimated diffusion coefficients in PET in contact with water.

Figure 1 displays some experimental diffusion coefficients for migration from PET into 3 % acetic acid, together with the D* correlations in PET films and in PET/ethanol systems. No data are available for DMSO (which could not be extracted from the test medium) and for all surrogates which are insoluble in water, as their migration was not detectable. In order to obtain overestimated D* for water, the two molecular weight zones must again be distinguished.

- For $80 < M < 130$ g/mol, a plateau is taken as a reference, corresponding to equation (4):

$$\log D_{\text{PET/aqu}, M < 130}^* = -12.7 \quad \text{equation (4)}$$

This corresponds again to the diffusion coefficient of 2,4-pentanedione, the fastest of our surrogates.

- For $M > 130$ g/mol, a single experimental diffusion coefficient (benzophenone) is available for migration into water. To obtain a $\log D^*$ correlation for water, we used the available knowledge on swelling effects: the more a polymer is swollen, the larger is the slope of the $[\log D^* = f(M)]$ correlations [7, 8].

Available experimental D values for migration into water (table 1) are only slightly larger than for diffusion in films, and far lower than for migration into ethanol. This shows that water plasticizes only slightly PET, and much less than ethanol. For further discussion, see reference 4. The slope of the $[\log D_{PET/aqu, M > 130}^* = f(M)]$ correlation (not observed) for water should be intermediate between those of PET plasticized by ethanol and of virgin PET:
 Slope of $[\log D_{PET/PET, M > 130}^* = f(M)]$ (equation 2) < slope of $[\log D_{PET/aqu, M > 130}^* = f(M)]$ (not observed) < slope of $[\log D_{PET/EtOH, M > 130}^* = f(M)]$

Therefore, the assumption that the slope for water (unknown) is the same as that for ethanol (figure 1) is certainly an additional overestimation of the D^* values into water. The overestimated D^* is then given by equation (5):

$$\log D_{PET/aqu, M > 130}^* = 0.0148 M - 10.77 \quad \text{equation (5)}$$

We must recognize this is probably a severe overestimation: the diffusion behaviour in PET in contact with an aqueous simulant is probably close to virgin PET. This can be seen with the only experimental data we obtained for $M > 130$ g/mol: for benzophenone, the ratio between the overestimated and the real value is 21. Moreover, the higher is M , the higher is the overestimation. Nevertheless, since we use in this work diffusion data which are very realistic (obtained for low surrogate concentrations), and even with pessimistic values for high molecular weights the conclusions should be quite satisfactory for consumers protection.

IV. Simulation of overestimated migration from PET bottles with a functional barrier.

In this section, we will assume that bottles are filled immediately after processing, and we neglect any possible diffusion of pollutants from the recycled layer into the functional barrier before filling. This is a reasonable assumption in the case of PET, as we have shown that little diffusion occurs into the functional barrier of preforms during processing [6].

For a calculation of migration, several parameters have to be introduced in the software to calculate migration. If we turn to overestimated migration, calculated from overestimated parameters, five parameters are important.

- $D_{PET/PET}^*$, the overestimated diffusion coefficient in PET, is obtained from equations (2) and (3).
- $D_{PET/aqu}^*$ is the overestimated diffusion coefficient in PET plasticized by water. In principle, it changes with time, as the water plasticizes PET. In practice, since the diffusion of water is much faster than that of surrogates, D^* reaches very rapidly the equilibrium value, and $D_{PET/aqu}^*$ can be calculated from equation (4) and (5).

If more realistic (not overestimated) values are needed for some diffusants, they can be taken for instance from table 1, if the diffusants belong to the set of surrogates studied, or have a similar structure.

- C_{Food}^* , the tolerable concentration of pollutants in food is to be fixed by risk managers. It is related to the threshold of regulatory (or of toxicological) concern [19, 20, 21]. In Europe, values between 0.5 and 10 $\mu\text{g}/\text{kg}$ food are under discussion. In the calculations presented here, we will assume an average value of 1 $\mu\text{g}/\text{kg}$ food. The conclusions can be adapted to any other situation by a rule of three.

$C_{P,0}^*$ and t_{\max}^* , the two last parameters, are accessible to industry.

- Food industries decide about t_{\max}^* , the deadline of use of the recycled bottle. t_{\max}^* includes both the time of storage of the empty bottle and of the filled bottle. Diffusion into the functional barrier starts before filling the bottle. The software can take this into account, by using different steps. However, for very low migration levels, with the worst case assumptions used here, the influence of this storage time of the empty package is not important. It plays a significant role to predict migration over much larger storage times of the packaged food. This will be described in a dedicated paper.

- Packaging and recycling industries are able to influence $C_{p,0}$, the initial concentration of contaminants in PET, in order that it remains below $C_{p,0}^*$, the largest tolerable concentration of a pollutant in PET, through specifications or through purification of PET. Statistical studies showed that only 1 bottle on 10,000 is accidentally polluted [13, 22, 23]. In resins collected over Europe, three cases of misuse were identified, where pollutants were present at high concentrations (1.4 to 2.7 ppm) before processing, and limonene (a food aroma compound) reached 18 ppm. When the resins are submitted to a thermal treatment (“supercleaning” operations) [14, 24, 25], no pollutant has been detected in such a resin up to now. We will consider here three different values of $C_{p,0}^*$: 1 ppm (assuming this for a “cleaned” sample), 10 ppm (for a realistically polluted sample) and 100 ppm (as an unrealistic worst case).

Let us first consider a classical PET tri-layer bottle, with a 60 μm functional barrier, in contact with an aqueous medium. In a first pessimistic case we consider a pollution by very fast diffusing molecules, all with a very high initial diffusion coefficient $D_{PET/PET}^* = 7.7 \cdot 10^{-14} \text{ cm}^2/\text{s}$ (in virgin PET) (from equation 2). This diffusion coefficient increases to the value obtained in contact with water ($D_{PET/aqu}^* = 2 \cdot 10^{-13} \text{ cm}^2/\text{s}$, from equation 4). The corresponding simulated migration kinetics are presented on figure 2. The concentration in food is normalised to the initial concentration of pollutant in recycled PET. This representation allows to calculate the bottle life time t_{max}^* for different initial concentrations in recycled PET: for example, if risk managers decide that the maximal tolerable migration is 1 $\mu\text{g}/\text{l}$, the lifetime of a bottle is 181 days, for an initial concentration of 100 ppm. For an initial concentration of 10 ppm, it is 372 days. These results show that even in exaggerated overestimated conditions (40°C, high initial concentrations, highest diffusivity), migration remains at very low levels after one year, which often corresponds to the limit date of consumption.

Using figure 2, the maximum time of use of the materials consistent with other tolerable / regulatory migration levels of pollutants can be determined with a rule of three. For example, at $t = 181$ and 372 days, the migration level is 0.1 $\mu\text{g}/\text{l}$ for an initial concentration of 10 ppm and 1 ppm respectively.

Influence of the recycling process

During the recycling process, volatile pollutants may be more or less evaporated. Let us consider now a recycling process which removes all volatile molecules until a given molecular weight (this situation does of course not exist, as volatility is not only a function of M). In Figure 3, the maximum tolerable initial concentration in the recycled part of a bottle is given as a function of molecular weight, for two different lifetimes: 6 months and 1 year. Figure 3 has been obtained by calculating different migration kinetics from different couples of $D_{PET/PET}^*$ (equations 2 and 3) and $D_{PET/aqu}^*$ (equations 4 and 5). The previous situation (for low M) is found again with the two plateau values at 100 and 10 ppm for 6 months and 1 year of lifetime respectively. Above 130 g/mol, the tolerable amount increases exponentially with M . For example, these concentrations could reach 10,000 ppm for $M = 175$ g/mol and lifetime of 1 year, or for 155 g/mol and lifetime of 6 months. Such a high initial concentration is of course totally unrealistic. This illustrates how critical can be the benefits of removal of low molecular weight compounds, using a suitable recycling process. This also supports authorities which assess the safety of a recycling process by its capacity to eliminate chemicals of concern (mainly the more volatile compounds), rather than by testing a finished bottle.

Influence of the thickness of the functional barrier.

A 60 μm thick functional barrier protects food at least 1 year from contamination (considering a maximum initial concentration of 10 ppm). If the initial concentration of the pollutant in recycled PET part of the bottles is lower, then it could be envisaged to reduce the functional barrier thickness.

Figure 4 shows the minimal functional barrier thickness needed to have less than 1 $\mu\text{g/l}$ migration after 1 year of contact with aqueous food, for the highest $D_{PET/aqu}^*$ value (equation 4). Figure 4 has been obtained calculating different migration kinetics from different functional barrier thicknesses. Once more, the most pessimistic situation is considered: $80 < M < 130$ g/mol pollutant. The previous situation corresponding to a 60 μm thick functional barrier is found again (initial concentration = 10 ppm). The minimal thickness is increasing regularly and slowly above 10 ppm. It means that a small increase of the thickness allows an important increase in the initial tolerable concentration $C_{P,0}^*$ of pollutants in PET. On the other hand, for concentrations lower than 10 ppm, the minimal thickness decreases drastically when

the initial tolerable concentration decreases. The extreme situation is the case of a direct contact of the recycled layer with the food.

The recycling of PET using a functional barrier thus appears to protect efficiently food from undesired pollutant migration. More data about the real level of pollution (statistics) in the collected mass of PET bottles have to be acquired to confirm that the level of 10 ppm is totally unrealistic. Moreover, if authorities decide that the maximal tolerable migration level for unknown substances is different from 1 $\mu\text{g/l}$, the corresponding tolerable concentration in recycled PET could be recalculated by a rule of three and applied to the new situation.

Another possibility for recycling is to use recycled PET in direct contact with food. We can evaluate this situation, with help of both our experimental results (real migration tests with model monolayer bottles entirely made of deliberately polluted PET) [5] and of numerical simulation of migration, using the overestimated diffusion coefficients.

V. Simulation of overestimated migration from recycled PET bottles in direct contact with food.

We have seen in the previous section that the minimal thickness of a functional barrier can be determined in function of the initial amount of pollutant in recycled PET. If we consider now a thickness of functional barrier equal to zero, we describe the behaviour of a recycled bottle in direct contact with food.

As for tri-layer bottles, we overestimate the migration from monolayer bottles at 40°C and for a period of 1 year. Figure 5 is obtained from different migration kinetics; for different

$D_{PET/PET}^*$ and $D_{PET/aqu}^*$ couples and displays tolerable $C_{P,0}^*$ values.

The maximum tolerable initial concentration $C_{P,0}^*$ is 0.48 mg/kg for $M < 130$ g/mol pollutants, assuming, as previously, $C_{Food}^* = 1$ $\mu\text{g/l}$ as the maximum tolerable migration level. Again, as previously, the migration after one year can be calculated for another initial concentration, by

a rule of three. For example, for 10 ppm and $80 < M < 130$ g/mol, the migration should be 20.8 µg/l.

$C_{P,0}^*$ increases quickly for $M > 130$ g/mol, but much less than with a functional barrier. This means that a larger range of pollutants could reach a critical migration level C_{Food}^* and that the recycling/cleaning processes have to be more efficient for higher molecular weight compounds. For example, for $M=275$ g/mol, a maximum concentration of 10 ppm in bottles has to be ensured by industrial washing and drying processes. This concentration is larger than 1 000 000 ppm in the case of a 60 µm functional barrier.

The tolerable initial amount of pollutant above 130 g/mol follows an exponential relationship given by the following equation:

$$C_{P,0,direct\ contact}^* = 0.0237 \cdot \exp(0.022M)$$

The software used for the simulation of migration allows to take into account the progressive increase of diffusion coefficients with space and time, from $D_{PET/PET}^*$ to $D_{PET/aqu}^*$, as the result of plasticization due to water penetration. As we have seen, water diffusion is much faster than that of surrogates, and the upper $D_{PET/aqu}^*$ values are quickly reached; the system can then be approximated mathematically to the model case of a plane sheet, with a constant diffusion coefficient:

$$\frac{m_{F,t}}{A} = \frac{2}{\sqrt{\pi}} \cdot C_{P,0}^* \cdot \rho_P \cdot (D_{PET/aqu}^* \cdot t)^{0.5} \quad \text{equation 6}$$

where $m_{F,t}$ is the migrant quantity in the food at t time, A the area of packaging in contact with food, $C_{P,0}^*$ the maximum initial concentration in the packaging material, and ρ_P the density of material (reference...). Considering this linear approximation (for low conversion yields) of migration kinetics, the reference curve of figure 5 can be used to calculate maximum acceptable initial concentrations, considering another contact time than 1 year.

Overestimated migrations of potential pollutants into aqueous media after 1 year at 40 °C have been simulated for direct contact with recycled PET and for contact with a functional barrier. It is now interesting to compare both situations in order to evaluate the interest of a

functional barrier. This comparison depends of course on the molecular weight of the pollutant but also of the time of storage (assumed to be the time of contact).

Figure 6 represents the ratios of migration from monolayer and trilayer (60 μm functional barrier) bottles respectively. The ratio curves for $80 < M < 130$ g/mol, $M = 150$ and 170 g/mol are given as a function of time.

It can be seen that the curve for $80 < M < 130$ g/mol gives the smallest ratio between the two kinds of bottles: the interest of a functional barrier is more important when the molecular weight of the pollutant increases. Even when the molecular weight is low, barrier properties are sufficient to ensure a good efficiency of the PET bottle with a functional barrier: for a migration period of 200 days for example, the bottle with functional barrier is at least 100 times more efficient than with a direct contact.

Even more interesting is the effect of maximum food storage time. After 1 year storage, taking the same example, the ratio falls to 22. The ratio being obviously lower for longer contact times, we can conclude that direct food contact is more interesting for long lifetime applications.

VI. Temperature effect on our results and overestimation of migration.

Official test conditions for monolayer materials recommend that a long term storage at ambient temperature is simulated by a 10 days test at 40°C . This is why we have conducted experimental determinations of D at 40°C [4]. In these tests, the temperature 40°C is in general larger than the actual storage temperature, which gives another safety margin to compensate for the short time of test. However, using modelling, it is now possible to address the actual time and the actual temperature of storage. In this section we examine the influence of temperature, in order to predict a more realistic behaviour of the materials. Indications will

be given on possible accelerated test conditions for materials with multilayers and with a functional barrier.

In a previous paper, we have shown a chart of activation energies of diffusion in function of M. This was a compilation of both literature data for gases (2 – 60 g/mol) and of our own experimental data with surrogates (M > 80 g/mol), measured in the 40-60 °C range [4]). The activation energy increases roughly with molecular weight, ranging from 20 KJ/mol for gases to around 150 kJ/mol for 200 g/mol diffusants. The boundary between gases and surrogates is observed around 80 kJ/mol. Data obtained for other polymers suggest that this value is quite general [26].

To predict migration at 25 or 30 °C from diffusion coefficients measured at 40 or 60 °C, we must keep a safety margin for the extrapolation to a lower temperature. This requires that a worst case activation energy is used, which is the lowest possible value (to be convinced, check that the assumption $E_a=0$ would give the same values at 25 °C as those measured at 40 °C). We propose here to use the value $E_a = 80$ kJ/mol for the surrogates.

Using this value for activation energy, the ratio between diffusion coefficient at 40 or 60 °C and room temperature depends on the value chosen to overestimate “room temperature”.

Ratios are given in table 2.

For example, at 30°C, for pollutants in the $80 < M < 130$ g/mol range (initial concentration in PET 1 ppm), for a storage time of 1 year, and with a 60µm thick functional barrier, the calculated migration is 0.0043 µg/l in contrast to the 0.0944 µg/l calculated at 40°C.

Migration is then at least 21 times lower than the one at 40°C. In the case of a bottle with a functional barrier, the migration decrease depends on the time of contact: the reducing factor can then be much higher than 21. It can be seen that this does not lead to an evaluation of safety of consumers which would reduce the safety margin.

For a material in direct contact of the recycled material with food, when the same simulation is done, the gap between the 2 migration temperatures is lower: $1.6 = \sqrt{2.7}$. This results is obviously in agreement with equation 6. Looking at equation 6, for shorter contact times (less than 1 year), the effect of temperature decrease on the migration of a monolayer material, leads to a constant reduction factor (1.6).

Proposal for testing functional barriers

Testing functional barriers cannot be realised with the classical time / temperature conditions used for multilayers, for several reasons: (i) the lag time for migration may be higher than the recommended time of test (the largest test time recommended in 97/48 directive is 10 days, while we have seen in this paper much larger lag times); (ii) glassy polymers require very long times of testing, so that it is preferable to use modelling and (iii) the error made with a 10 days test can be much larger with multilayers than with monolayers.

On the basis of results presented here, it is possible to propose the principle of accelerated tests, both for ageing PET multilayer bottles (diffusion from the recycled layer into the functional barrier before filling the bottle) and for monitoring migration. Equivalencies between time of test at 60 °C and actual conditions of use can be calculated using the worst case activation energy, as in Table 2. From 60 °C to 25 °C, a 30 fold acceleration factor is obtained.

These acceleration factors proposed in table 2 are again overestimating actual migration at ambient temperature, as the real activation energy can be larger. More realistic values can be used if they are available and they would tend to reduce the overestimation.

CONCLUSION

Taking into account surrogates diffusion data determined previously, we proposed an empirical equation for the overestimation of pollutant diffusion coefficients in virgin PET at 40°C, as a function of the molecular weight of the considered molecule. These parameters are obtained with many overestimating assumptions, and they are heavily on the side of the protection of public health: only the top of the experimental uncertainty range of D values has been taken into account, then the largest of these values were taken as reference diffusion coefficients, and the slope of the $[\log D = f(M)]$ correlation for water has been assumed to be equal to that of ethanol, which plasticizes PET. As very low molecular weight pollutants are

not likely to be present in recycled packaging, an upper bound value of pollutant diffusion coefficients was proposed, taking into account very fast diffusing molecules.

An equation is proposed to determine overestimated diffusion coefficients of surrogates in PET in contact with aqueous food simulants. As experimental diffusion data were not sufficient in this case, we used diffusion data in the case of ethanol contact to underestimate the barrier property increase with M , in the case of a contact with aqueous simulant.

These empirical equations have been used to simulate the migration into monolayer bottles, into multilayer bottles with different geometries of functional barrier, as a function of pollutant molecular weights. The effects of the different factors have been studied, and the interest of the functional barrier technology have been discussed (compared to direct food contact) as a function of food contact time. The food packaging contact time is an important factor: functional barriers are very efficient for short contact times, even when the initial concentration of pollutant in food is important, and even when fast molecules are considered. The technology can be used without purification steps on the PET resin. But for high contact times (more than one year), direct food contact (which requires to ensure low initial pollutant amounts) becomes interesting.

It is proposed that a simulation of real time of storage at ambient temperature (25-35 °C) could replace the 10 days at 40 °C and it has been shown to be even more severe. The choice of an activation energy to extrapolate calculated migration data from 40°C to ambient temperature was discussed. Depending on the value of the “room temperature” (from 30 to 20°C), diffusion coefficient is reduced by a factor 2.5 to 7. Depending on the type of recycled bottle, the impact of temperature decrease is different (higher decrease of migration from bottles with a functional barrier).

Apart from our systematic study of the variable effects, we can remark that using realistic initial pollution levels, most of the situations of migration from PET bottles lead to very low levels of migration which permits to be optimistic for the use of PET in recycling applications.

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Nr	Surrogates	M (g/mol)	$D_{PET/PET}$ at 40°C	$D_{PET/aqueous}$ at 40°C	$D_{PET/EtOH}$ at 40°C	$D_{PET/aqu}^*$ at 40°C	$D_{PET/aqu}^*$ at 25°C
1	Dimethyl sulfoxide (DMSO)	78	$5.0 \cdot 10^{-14}$	-	$2.7 \cdot 10^{-12}$	$2.0 \cdot 10^{-13}$	$4.7 \cdot 10^{-14}$
2	Toluene	92	$3.8 \cdot 10^{-14}$	$9.5 \cdot 10^{-14}$	$4.8 \cdot 10^{-12}$	$2.0 \cdot 10^{-13}$	$4.7 \cdot 10^{-14}$
3	Phenol	94	$3.0 \cdot 10^{-14}$	$9.0 \cdot 10^{-14}$	$1.3 \cdot 10^{-12}$	$2.0 \cdot 10^{-13}$	$4.7 \cdot 10^{-14}$
4	2,4-Pentanedione	100	$7.7 \cdot 10^{-14}$	$2.0 \cdot 10^{-13}$	$2.2 \cdot 10^{-11}$	$2.0 \cdot 10^{-13}$	$4.7 \cdot 10^{-14}$
5	Chlorobenzene	113	$4.4 \cdot 10^{-14}$	$1.3 \cdot 10^{-13}$	$3.2 \cdot 10^{-12}$	$2.0 \cdot 10^{-13}$	$4.7 \cdot 10^{-14}$
6	Nonane	128	$2.7 \cdot 10^{-16}$	-	$5.0 \cdot 10^{-13}$	$2.0 \cdot 10^{-13}$	$4.7 \cdot 10^{-14}$
7	1,1,1-Trichloroethane	133	$2.8 \cdot 10^{-16}$	-	$2.5 \cdot 10^{-13}$	$1.8 \cdot 10^{-13}$	$4.2 \cdot 10^{-14}$
8	Chlorooctane	149	$1.8 \cdot 10^{-15}$	-	$2.7 \cdot 10^{-13}$	$1.0 \cdot 10^{-13}$	$2.4 \cdot 10^{-14}$
9	Phenylcyclohexane	160	$8.4 \cdot 10^{-18}$	-	$5.0 \cdot 10^{-14}$	$7.2 \cdot 10^{-14}$	$1.7 \cdot 10^{-14}$
10	Ethyl Hydrocinnamate	178	$8.6 \cdot 10^{-17}$	-	$6.0 \cdot 10^{-13}$	$3.9 \cdot 10^{-14}$	$9.0 \cdot 10^{-15}$
11	Benzophenone	182	$8.1 \cdot 10^{-17}$	$1.5 \cdot 10^{-15}$	$1.0 \cdot 10^{-13}$	$3.4 \cdot 10^{-14}$	$7.8 \cdot 10^{-15}$
12	Azobenzene	182	$1.9 \cdot 10^{-16}$	-	$7.6 \cdot 10^{-14}$	$3.4 \cdot 10^{-14}$	$7.8 \cdot 10^{-15}$
13	Phenyl benzoate	198	$1.2 \cdot 10^{-16}$	-	$7.0 \cdot 10^{-14}$	$2.0 \cdot 10^{-14}$	$4.5 \cdot 10^{-15}$
14	Methyl palmitate	270			$3.5 \cdot 10^{-14}$	$1.7 \cdot 10^{-15}$	$4.0 \cdot 10^{-16}$
15	Dibutyl phthalate (DBP)	278			$5.3 \cdot 10^{-15}$	$1.3 \cdot 10^{-15}$	$3.0 \cdot 10^{-16}$

Table 1: largest experimental values of diffusion coefficients of surrogates at 40°C

$D_{PET/PET}$ is the diffusion coefficient in film/film experiment (usually D_{33} in [4])

$D_{PET/aqueous}$ is for migration from bottles into 3 % aqueous acetic acid (usually $D_{Aq, tri}$ in [4])

$D_{PET/EtOH}$ is for migration from bottles into ethanol (usually $D_{Et, mono}$ in [4])

$D_{PET/aqu}^*$ at 25 and 40°C are overestimated values

Temperature of actual use	Acceleration factor from test at 40 C	Acceleration factor from test at 60 C
20 °C	8.1	51.8
25 °C	4.7	29.8
30 °C	2.7	17.5
35 °C	1.6	10.4

Table 2: Acceleration factors of D in function of the accelerated test temperature, using an activation energy of 80 kJ/mol

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Figure 1: Evolution of diffusivities of surrogates at 40°C with molecular weight in virgin PET (■), in PET plasticized by aqueous simulant (○), and in PET plasticized by ethanol (monolayer bottles, ▲). Experimental data are taken from [4]. Equations given in text for overestimation of diffusion coefficients at 40°C correspond to straight lines.

Figure 2: Determination of the largest time of use of a bottle with a 60 μm functional barrier by simulation of worst case migration kinetics at 40°C (overestimated migration for lower molecular weight, $80 < M < 130$ g/mol). Kinetics are normalised with the initial concentration of potential pollutant in the recycled part of the bottle.

A: corresponds to a $C_{\text{food}}=1\mu\text{g/l}$, for $C_{P,0}=100$ ppm in the inner layer

B: corresponds to a $C_{\text{food}}=1\mu\text{g/l}$, for $C_{P,0}=10$ ppm in the inner layer

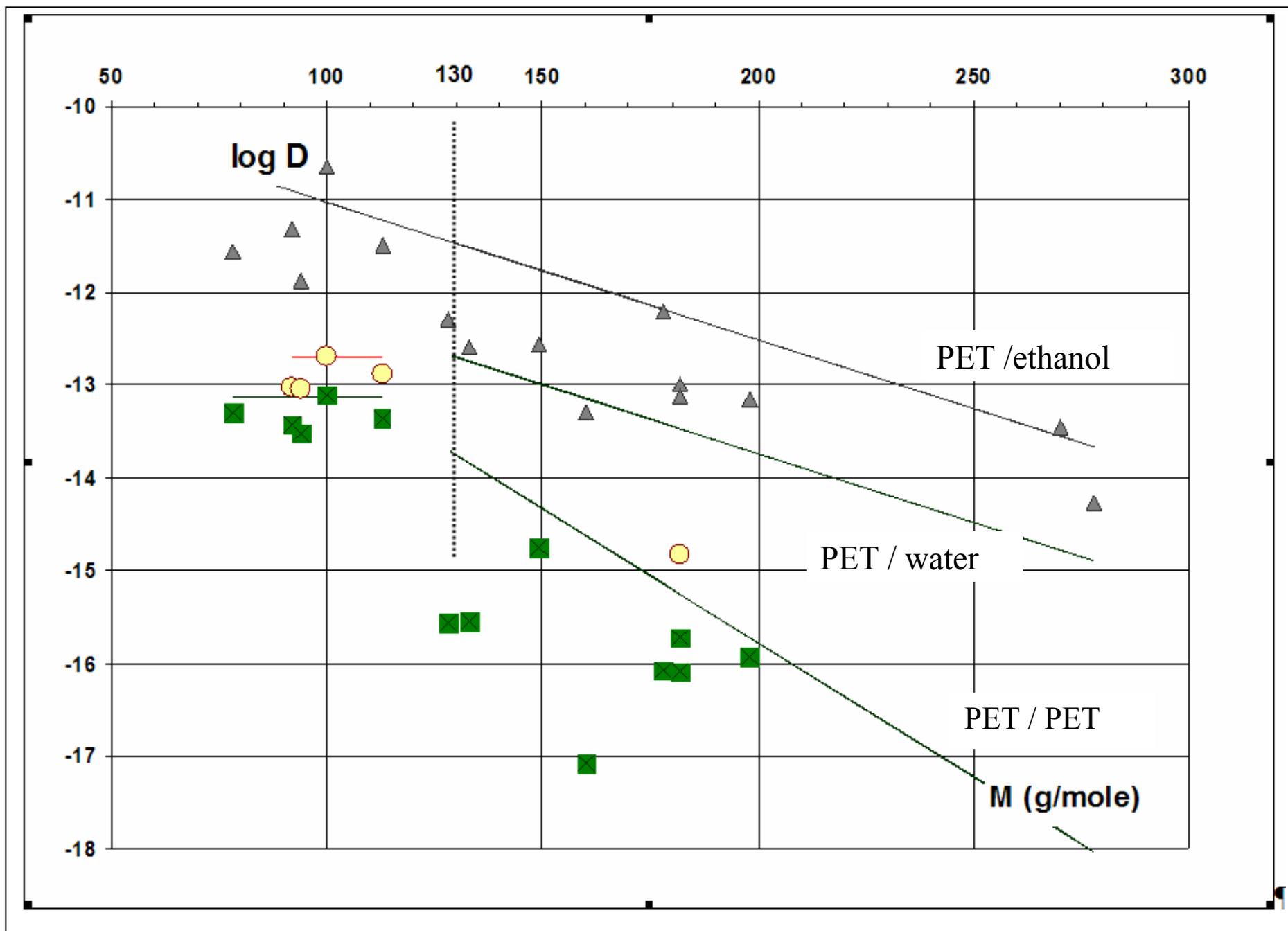
Figure 3: Maximum initial concentrations of potential pollutants in the recycled part of a bottle with 60 μm functional barrier in order to reach a 1 μg/l migration in aqueous simulant at 40°C after 6 months (■) and 1 year (●). These initial concentrations are obtained from simulations of overestimated migration in function of molecular weight. Each symbol corresponds to simulated kinetics as obtained in figure 2.

Figure 4: Determination of the minimal thickness for a functional barrier to get a migration of 1 μg/l in aqueous simulator at 40°C after 1 year, in function of the initial concentration in the recycled part. Overestimated results are obtained by simulation with different thickness of functional barrier, and using overestimated parameters. Each symbol corresponds to simulated kinetics as obtained in figure 2.

Figure 5: Maximal initial concentration of potential pollutants in recycled PET in direct contact with aqueous simulant at 40°C to get a migration of 1 μg/l after 1 year, in function of the molecular weight. Each symbol corresponds to simulated kinetics as obtained in figure 2.

Figure 6: Comparison of simulation of overestimated migration of potential pollutants at 40°C in aqueous simulant from a monolayer bottle and from a bottle with a 60 μm functional barrier. Comparison are made for the same concentration in the recycled part of each kind of bottles and for 3 molecular weight: $M < 130$ g/mol(●), $M=150$ g/mol(■) and $M=170$ g/mol(▲). Each symbol corresponds to simulated kinetics as obtained in figure 2.

Figure 1



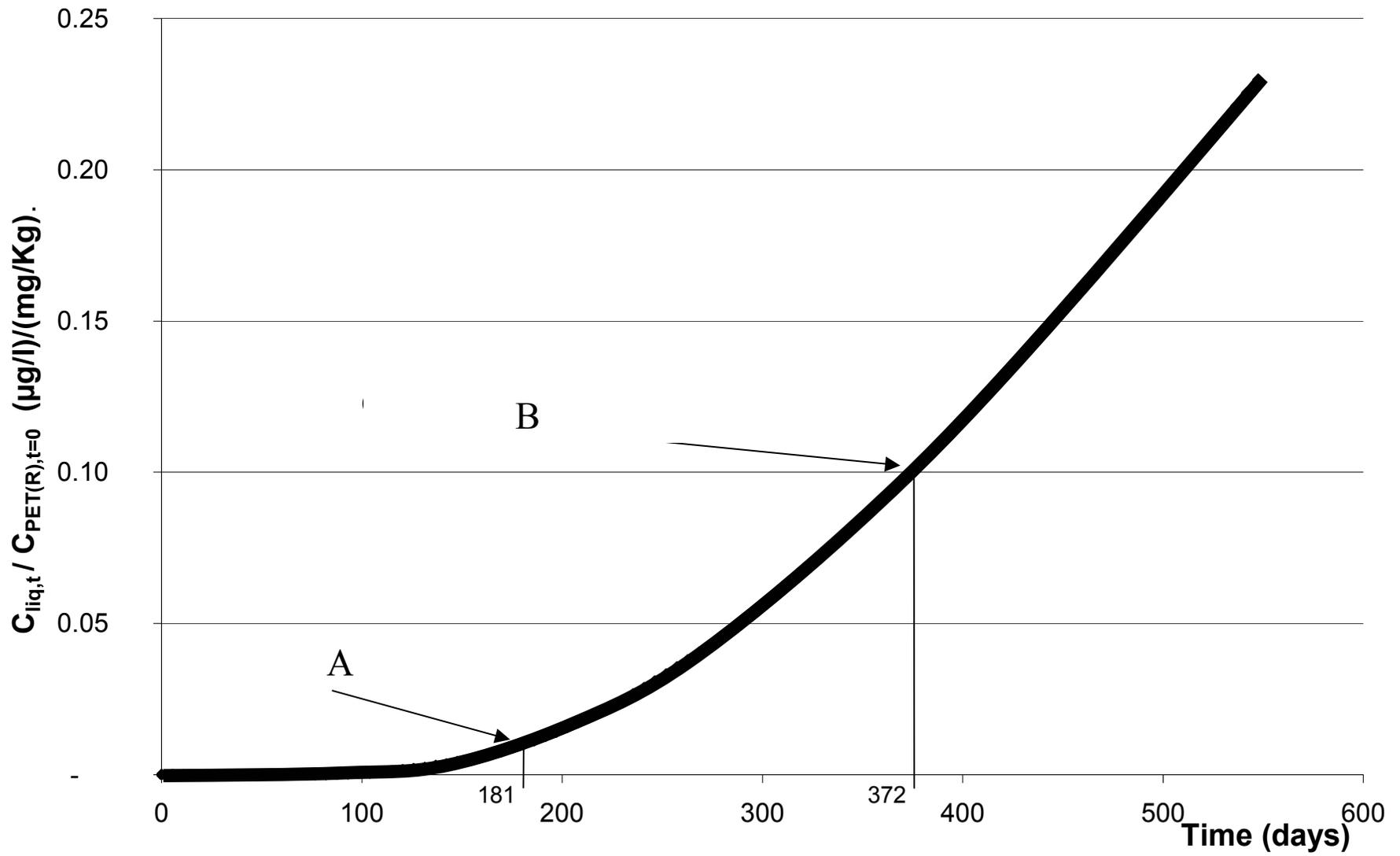


Figure 2

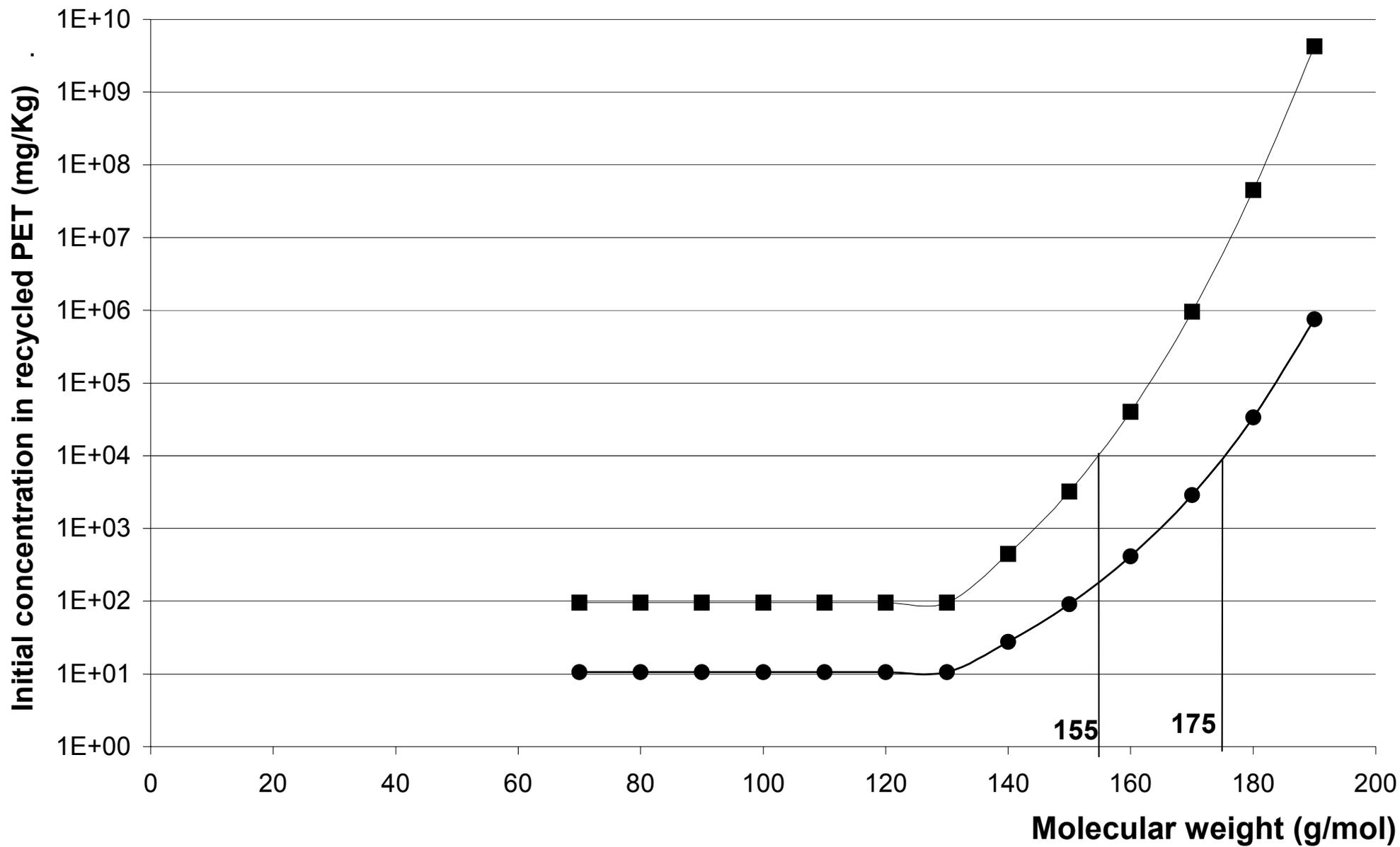


Figure 3

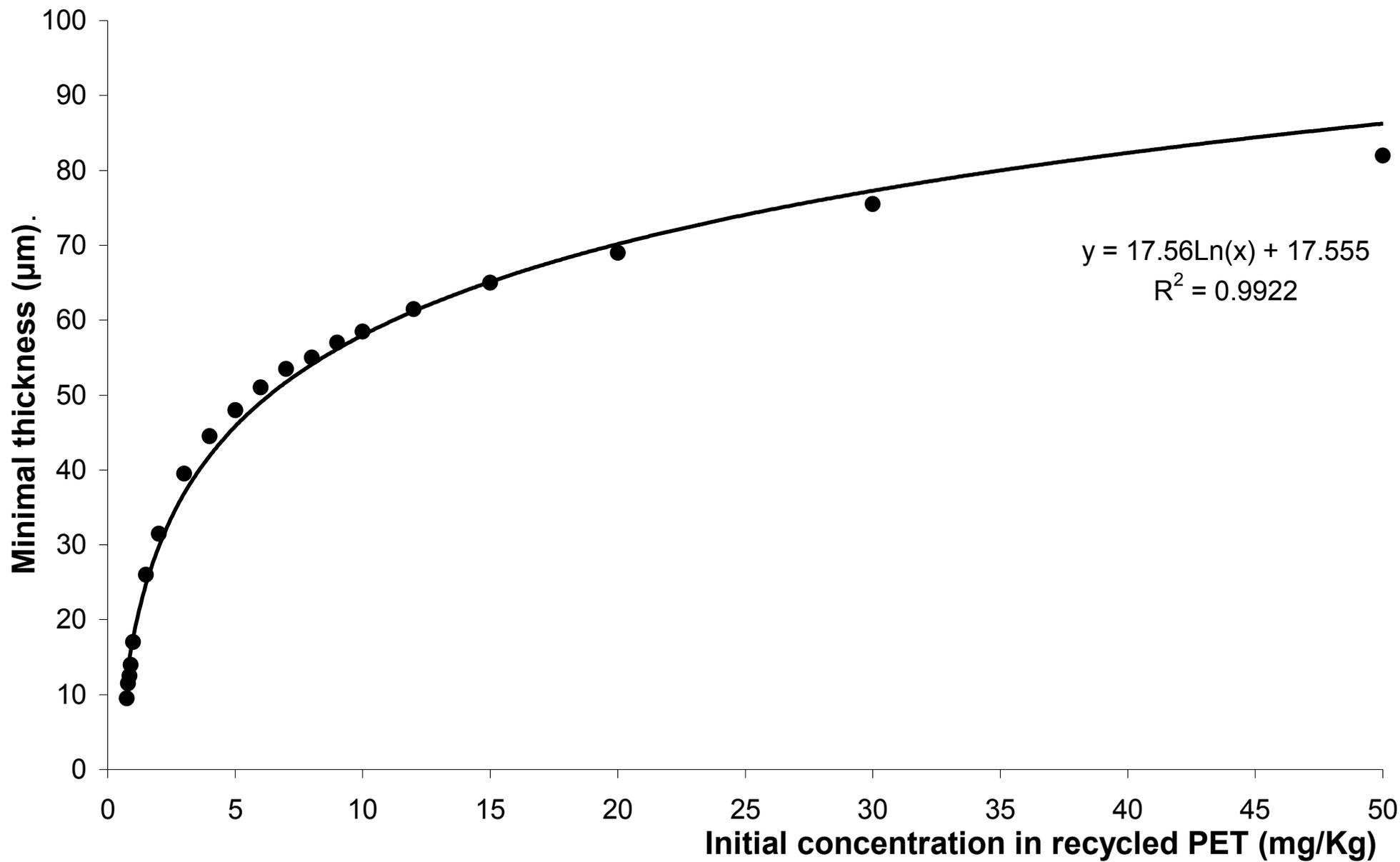


Figure 4

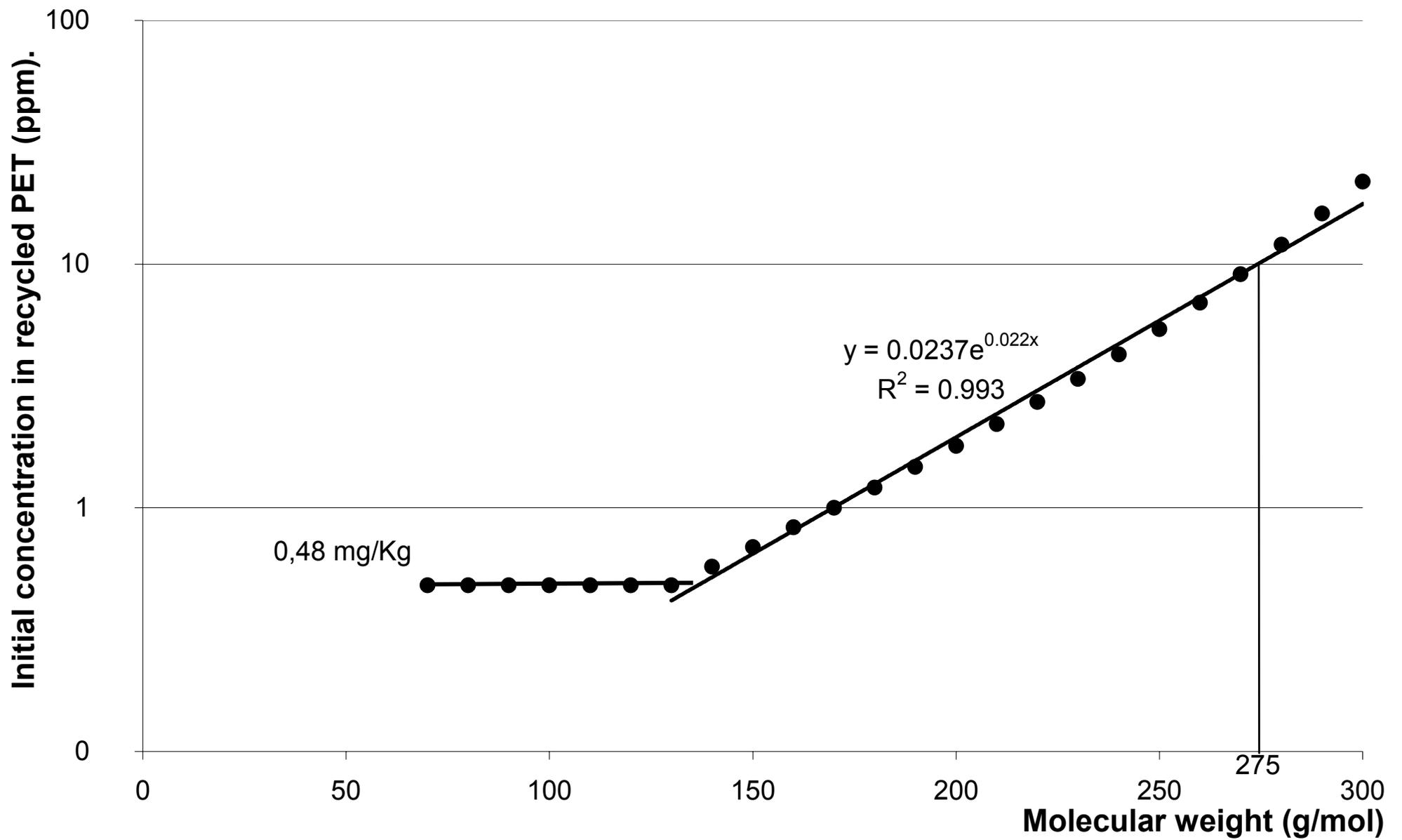


Figure 5

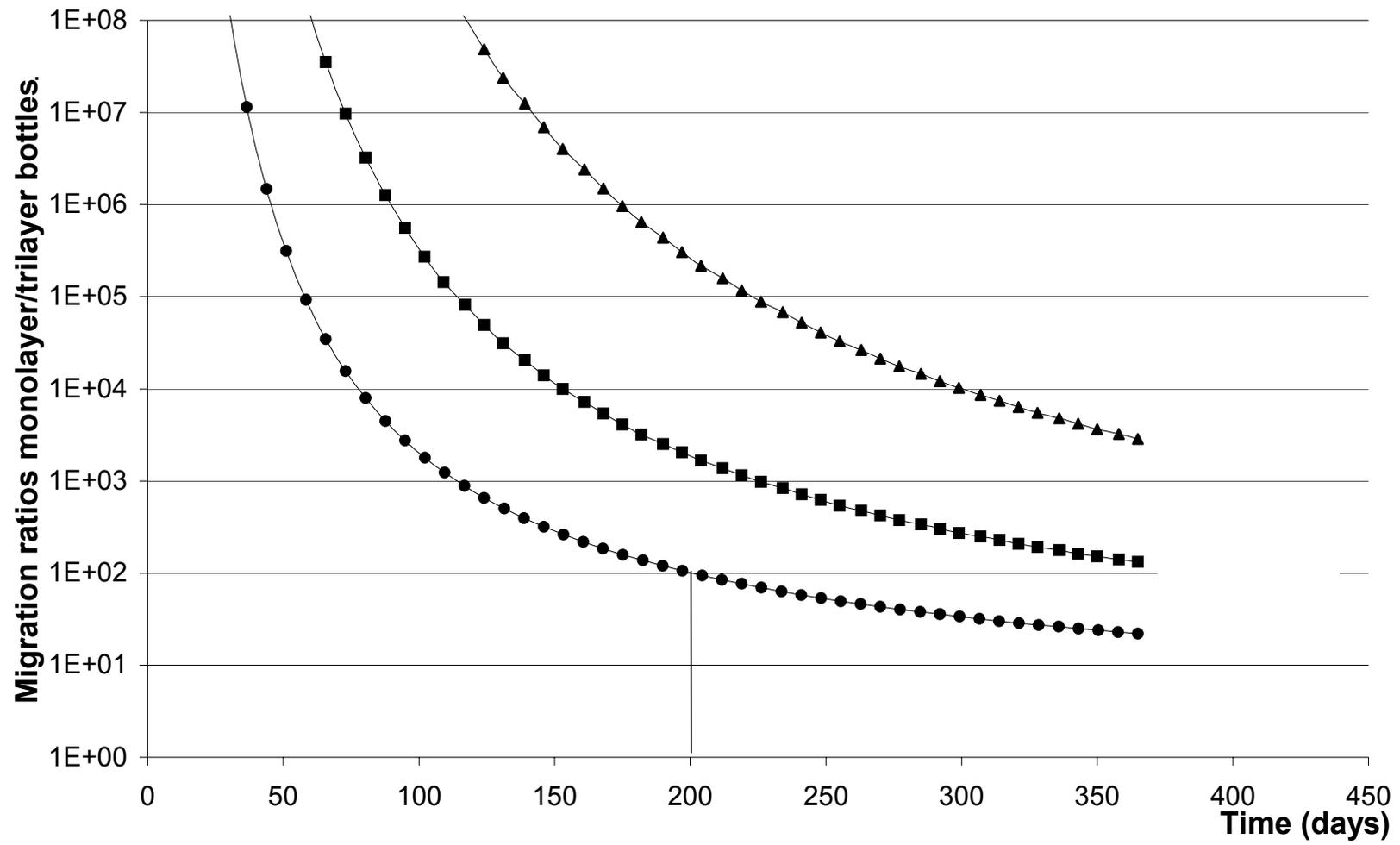


Figure 6