Determination of Mass Transport Properties in Food/Packaging Systems by Local Measurement with Raman Microspectroscopy

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ABSTRACT: A fast, nondestructive method based on the determination of local concentration profiles in the polymer thickness with Raman microspectroscopy is presented here. It was used to assess the diffusivity of a model molecule (p-terphenyl) in amorphous polystyrene films at 95°C ($2.38 \pm 1.08 \times 10^{-17}$ m²/s). This methodology was validated by comparison with a more classical destructive approach based on the monitoring of the concentration evolution in the whole of the film with gas chromatography (89.4×10^{-17} m²/s). These values were in agreement with data available in the literature for molecules of the same molecular weight and temperature range determined with local measurement and were significantly lower than those determined by global measurement. Raman microspectroscopy was found to be adapted to slow diffusion speeds typically found in high-barrier polymers; this allowed diffusivity to be obtained long before the equilibrium was reached and, thus, without the need for the partition coefficient. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40958.

INTRODUCTION

Food contact materials (FCMs) must comply with European regulation 1935/2004, which can be summed up in two main requirements. Packaging materials shall not transfer their constituents to food in quantities that could (1) endanger the human health and (2) bring about deterioration in organoleptic characteristics. To ensure the safety of consumers, European regulation 10/2011 translates the requirements of regulation 1935/2004 to plastic materials and lays down the procedure for their compliance. In addition to the requirement of inertia for plastic FCMs, regulation 10/2011 provides guidelines on the testing procedure for migration assessment. An important aspect of the regulation is that it allows the use of "generally recognized diffusion models based on experimental data [...] under certain conditions" to determine overestimated migration levels and to prevent expensive and time-consuming experiments. In this way, the existing models used to describe migration are based on the Fickian diffusion equation, which involves at least two key parameters: (1) the diffusion coefficient, or diffusivity (D), and (2) the partition coefficient (KPL). Little attention has been paid though to the assessment of the KPL, and a commonly accepted approach is the use of a KPL value of 1 if the migrant is soluble in the food or 1000 otherwise.[1] In contrast to KPL, D

must be determined for each polymer–migrant couple because it depends on physical characteristics of both (molecular mass, molecular volume, polarity of the diffusing molecule, and glassy or rubbery state of the polymer matrix). In addition to experimentation, D can be determined via predictive modeling, which is generally based on empirical or semiempirical relationships such as the ones developed by Piringer[2] and more recently by Welle.[3] Special attention should be paid to Piringer semiempirical relationship, which does not try to accurately predict but instead tries to give the worst case scenario D values. This strategy, based on purported overestimation, has proven to be an efficient strategy for the safety evaluation of FCMs, but it may be inappropriate in other cases, such as the plastics decontamination inherent to the recycling process. In this case, overestimation of the D values of migrants could lead to an overestimation of the efficiency of the decontamination, which would endanger consumer health. The experimental determination of D remains, therefore, indispensable for the reliable prediction of migrant diffusion within the polymer.

The experimental determination of D consists of two steps: (1) monitoring the diffusion of a molecule through a polymer resulting from the imposition of a concentration gradient and (2) identification of the D value from the experimental data by

comparison with a mathematical model with a dedicated optimization algorithm. The experimental data can be of two kinds, depending on the analytical technique used to monitor the migrant: (1) a concentration profile as a function of the polymer thickness (local measurement or local profiling) and (2) the average concentration in the whole film as a function of time (global measurement, global concentration evolution, or global kinetics). The identification of a D value necessitates that the equilibrium be reached or that the KPL between the polymer and the medium in contact with it be known. Because KPL data is scarce and because of the time required to reach equilibrium for high-barrier polymers, the determination of D in the latter is made difficult. As consequence, most published D values have been collected for polymers that are rubbery at room temperature.[4–11] Rare D values exist for the two high-barrier polymers most used in the packaging industry [polystyrene (PS) and poly(ethylene terephthalate)], and they are often for low- to medium-molecular-weight and presumably highly volatile molecules. In the case of amorphous PS, reported D values concern cyclohexane (86.2 g/mol);[12] linear alkanes (from 114.3 to 226.4 g/mol);[13] carboxylic acids (from 60.1 to 256.4 g/mol);[14] alcohols (from 32 to 242.4 g/mol);[15] toluene (92.4 g/mol), chlorobenzene (112.6 g/mol), and phenyl cyclohexane (160.26 g/mol);[16] homologous series of fluorescent tracers (from 230 to 1120 g/mol);[17] and Rubrene (532.7 g/mol),[18] with the majority of values being determined in the rubbery state. More abundant is literature on poly(ethylene terephthalate)[19,20] (several molecules with different functional groups from 78 to 431 g/mol[21] and several molecules with different functional groups from 92.4 to 298.5 g/mol), among others.

Some of these approaches make it possible to determine D in a faster, nondestructive way, by obtaining local concentration distribution profiles through the thickness of the material. For example, noninvasive fluorescence recovery measurement after photobleaching (FRAP) techniques (fluorescent recovery after photobleaching) has proven to be well adapted to the investigation of the diffusion of high-molecular-weight surrogates in high-barrier polymers, but it is limited to the transport of fluorescent molecules.[22] Applied to a specifically designed set of model probes ranging from 230 to 1100 g/mol, the FRAP technique was used to determine the diffusion (reaching 10^{-19} m²/s) into amorphous PS.[15] The second example of a promising nondestructive method is Raman microspectroscopy, which has turned out to be a powerful method to provide spatially resolved information about the chemical composition of materials. With confocal collection optics, the method is well suited to the characterization of diffusion in rubbery polymers.[23] In this study, it permitted us to determine D in the studied polymer with less than 24 h of contact with the food simulant after one profile acquisition that took 4 h, whereas the determination of D with the classical method based on a global average profile required 26 days to obtain the full kinetics as a function of time.

The objective of this study was to explore the potential of Raman microspectroscopy as an analytical device adapted to the fast characterization of the mass transport properties of molecules in high-barrier polymers in the glassy state for which diffusion speeds are usually very slow. p-Terphenyl was selected as the model molecule to follow the diffusion phenomena in amorphous PS in glassy state. A Moisan test was used as an experimental setup to induce the mass transfer phenomena in the virgin PS films. Raman microspectroscopy was used to determine the local concentration profiles through the thickness of the polymer after a given contact time. The D value identified from the local distribution profile was compared to that determined by the global evolution concentration measurement assayed by gas chromatography (GC) analysis. The difference in the resulting D values was discussed in terms of the usability and relevance of each method.

EXPERIMENTAL

Chemicals

Amorphous PS, with a molecular weight of approximately 285,000 g/mol and a glass-transition temperature (case II transition) of approximately 105°C, was purchased from Polyone France. Ultralow-molecular-weight polyethylene (ULMWPE), with a dropping point around 115°C, was kindly provided by TER France. p-Terphenyl (purity ≥ 99.0%; CAS number 92–94-4), with a molecular weight of 230.3 g/mol, and the internal standard butyl hydroxyl toluene (BHT; purity ≥ 99.0%; CAS number 128-37-0), with a molecular weight of 220.35 g/mol, were purchased from Sigma-Aldrich (France).

Fabrication of the Films and Sources

The virgin PS films were made by the thermoforming of PS pellets (in a hot press) at 200 bar and 165°C for 5 min. PS films with 0.5, 1, 2, and 4 wt % p-terphenyl were made by a solvent-casting method. We solved the PS pellets (0.2 g/mL) along with p-terphenyl in tetrahydrofuran and spread them onto a Plexiglas surface. Sources of 0.5, 2, and 10 wt % p-terphenyl ULMWPE were made by the mixture of ULMWPE pellets with p-terphenyl at 135°C with a 5-cm Petri dish as a mold. Liquid wax and p-terphenyl were mixed by manual stirring and left to solidify. p-Terphenyl pellets were made by the pressing of p-terphenyl powder at 7.5 ton with an evacuable pellet die purchased from Eurolabo (Paris, France). The PS film thickness was measured with a micrometer (Braive Instruments, Chécy, France) in quintuplicate.

Diffusion Assay

Diffusion assays of p-terphenyl from a spiked ULMWPE source and a pure p-terphenyl pellet placed in contact with the virgin PS film were conducted by the Moisan method[16,24,25] at 95°C. Before each measurement, the PS film was removed and wiped with ethanol. Raman measurements were performed once after 72 h of contact with the pellet and after 30 days of contact with ULMWPEs spiked at three different concentration levels (0.5, 2, and 10 wt %). The GC measurements were done after 4 h, 17 h, 24 h, 48 h, 72 h, 1 week, 2 weeks, 3 weeks, and 4 weeks of contact with a 0.5 wt % ULMWPE source. PS films in contact with the source had to be replaced after each GC measurement because of the destructive nature of the method.

Raman Measurement

p-Terphenyl concentration profiles were determined as follows. Thin slices of PS were prepared with a razor blade and stuck on a microscope slide. Raman spectra were recorded between

Raman shifts of 800 and 3500 cm^{-1} with a confocal Raman Almega microspectrometer (Thermo-Electron) with the following configuration: excitation laser 633-nm He–Ne, grating = 500 grooves/mm, pinhole = 25 μm, and 50× objective. The resulting spectra were the mean of two acquisitions of 25 s each. The measurements were carried in triplicate in the cross section of the sample with a spacing of 1 μm.

Raman Calibration

All pretreatments of the spectra were performed with an Omnic v7.3 (Thermo-Electron). Processing included (1) a multipoint linear baseline correction and (2) normalization according to the area of the PS specific band at 1452 cm^{-1} assigned to the CH$_2$ bending mode (δCH$_2$). The relative content of p-terphenyl was assessed according to the area of the specific band (1290 cm^{-1})[26] assigned to the interring C—C stretching band (vC$_4$–C$_7$, C$_{10}$–C$_{13}$).

Partial least squares (PLS) regression was applied to quantify the concentration of p-terphenyl in PS. The calibration procedure was performed on the basis of a 1290/1452 cm^{-1} area ratio, and the concentration of p-terphenyl in PS was established by repeated measurements of the spiked p-terphenyl/PS films at 0.5, 1, 2, and 4 wt % concentration levels with TQ analyst software (Thermo Fisher). The calibration performance was calculated as the multiple-regression coefficient and root mean square error (RMSE) of calibration. The RMSE was used to evaluate the goodness of fit according to eq. (1):

$$\text{RMSE} = \sqrt{\frac{(y_{\text{exp}} - y)^2}{N - p}} \qquad (1)$$

where y_{exp} and y are the experimental and predicted p-terphenyl concentration values, respectively; N is the number of measurements; and p is the number of identified parameters. Because, in this case, it was only used to evaluate the goodness of fit and not to identify any parameter of the model, p was equal to 0.

The ratio of the standard error of prediction to the standard deviation (RPD) was calculated with eq. (2):

$$\text{RPD} = \frac{\text{SD}_{\text{cal}}}{\text{RMSE}} \qquad (2)$$

where SD$_{\text{cal}}$ is the standard deviation of the p-terphenyl percentage in the calibration data set.

Additive Extraction and GC Measurement

PS films were dissolved under agitation in 5 mL of dichloromethane for 1.5 h, during which 80 μL of a solution of a 1 mg/mL solution of BHT was added. After that, PS was reprecipitated by the addition of 5 mL of ethanol under agitation for 30 min. To remove the PS that was still in the aqueous phase, the organic extract was place under N$_2$ gas to evaporate a small amount of dichloromethane. The reprecipitated PS was completely removed by filtration, and the aqueous extract was concentrated again under N$_2$ gas to reduce the volume of solvent to 2 mL.

A volume of 1 μL of organic extract was injected in an Agilent technologies 7890A GC instrument equipped with an Agilent automatic liquid sampler and an HP 5 column (30 m × 0.32 mm, film thickness = 0.25 μm, J&W scientific) and a flame

ionization detector (hydrogen = 30 mL/min, nitrogen =30 mL/min, air = 300 mL/min). Hydrogen was the carrier gas at a flow rate of 1.5 mL/min. The temperature was set at 250°C for the injector and 300°C for the detector. The temperature ramp of the oven ranged from 40 to 250°C at 4°C/min and maintained at 250°C for 15 min. The p-terphenyl concentration in the vial was determined by the ratio of the peak area of p-terphenyl to the peak area of the BHT, which was previously calibrated with solutions of known concentrations to take into account all stages in the extraction–reprecipitation process. The calculated response factor of the calibration was 0.93, and the extraction performance, calculated on the basis of the data points used on the determination of D, was 37 ± 4.4%.

Identification of D

The internal diffusion of a migrant in the packaging is given by eq. (3):[27]

$$\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2} \qquad (3)$$

where t is the time (s), x is the distance (m), C is the polymer concentration in the diffusing substance (Mass of the diffusing substance/Mass of the polymer), and D is the diffusivity of the molecule in the packaging (m^2/s). D was assumed to be independent of C, so the system was said to follow Fickian kinetics. Equation (3) could be solved with the initial and boundary conditions that applied to the case to obtain an expression for the concentration distribution. The analytical solutions of eq. (3) that were used in this study are given by eqs. (4) and (5).[28] Equation (4) is used when the thickness of the system is several orders of magnitude greater than the region of the system in which diffusion occurs or can be detected. This kind of solution (called a *semi-infinite* or *short-time solution*) is easily recognized because of the use of the error function (erfc) as a result of the integration of the original differential equation. It allows one to follow the evolution of a local concentration profile in time. Equation (4) represents the concentration evolution in time in the whole thickness of the film:

$$\frac{C}{C_\infty} = erfc\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (4)$$

$$\frac{C}{C_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{(2n+1)^2 \pi^2 Dt}{4L^2}} \qquad (5)$$

where L is the thickness of the film. The different conditions to which each solution applies can be observed by the variables present on them. Equation (5) lacks of the variable x (the position in the film) because the concentration distribution on the film is not taken into account. However, because the integration has been made with the system considered to be finite, it does take in to account the parameter L. In both solutions, C_∞ is the concentration of the diffusing substance at equilibrium, or the solubility limit of the diffusing substance in the diffusing medium is required. Both solutions describe the sorption kinetics into an originally virgin medium from a source or medium spiked with the diffusing substance.

The p-terphenyl D was identified from the experimental data by minimization of the sum of the squared residuals between the

experimental and predicted profiles and with an optimization method (the Levenberg–Marquardt algorithm, with an optimization routine predefined from MATLAB software). The RMSE was used to evaluate the goodness of the fit, according to eq. (1). Because one parameter was being identified (D), $p = 1$.

Estimation of the p-Terphenyl Solubility in PS

C_∞ of p-terphenyl in PS was determined by the assumption that the region immediately adjacent to the source reached equilibrium in a very short time. This way, the p-terphenyl/PS characteristic peak area ratio of the first point of several concentration profiles after 30 days of contact with the ULMWPE sources were measured with Raman spectroscopy and then converted into concentration units with the chemometric model detailed previously. To confirm that C_∞ was independent of the source concentration, sources spiked at three different p-terphenyl concentration levels (0.5, 2, and 10 wt %) were used. Three measurements were taken for each source concentration level to ensure repeatability.

Uncertainty Propagation and Impact on the Identified D Value

A Monte Carlo sampling was applied to obtain a 95% confidence interval of D for each one of the methodologies. The Monte Carlo sampling consisted of the addition of artificial noise to one or more of the variables used in the identification of D. One way to do this is to introduce variations on the variable subject of study within a certain interval that imitates the error that can be present in an actual measurement. This process is repeated many times, and each of these times, D is identified. At the end, a D distribution can be built, where the mean of the distribution would be the searched D, and the confidence interval is determined as those values that enclose 95% of the distribution around the mean. For determination from the local concentration profiles, artificial noise was added by the introduction of variations to the position of each experimental point within the interval ± 1 μm according to the resolution of the Raman microscope. In the case of determination from the concentration evolution in time, variations were introduced on C_∞ within the interval of the standard deviation derived from its determination. The process was repeated 10,000 times for each methodology. A Lilliefors test was applied to the parameter distribution to verify the hypothesis of D following a normal distribution. If the test was positive, the confidence intervals were calculated with the formula for a normal distribution. If any known probability distribution fit the data correctly, instead of a confidence interval, we provided the incertitude by manually discarding 2.5% of the upper and lower values.[29]

RESULTS AND DISCUSSION

Test Conditions

Because one of the goals of the study was to show that the local measuring methodology was well adapted to high-barrier polymers in the glassy state, amorphous PS, which is also well representative of the food-packaging industry, was selected. The polymer being in glassy state means that transfer occurs at very low speeds. A robust determination of D requires at least four data points and requires that the maximum resolution of the Raman microscope is 1 μm. This means that if the diffusing substance does not penetrate at least as deep as 4 μm, the D value found this way may not be representative of the process. To be able to get enough data points in a reasonable time, one must accelerate the diffusion by performing the test at a high temperature while the polymer remains in the glassy state. This explains our choice of 95°C.

Instead of using an actual additive present in commercial packaging, we carried out the study with a model molecule. p-Terphenyl was chosen because of its strong Raman signal even within the PS matrix.

The thickness of the PS films was also important for the correct application of the methodology in two ways. The first was an experimental limitation: above 350 μm, it became difficult to obtain a clean cut that could ensure usable concentration profiles. The second was related to the semi-infinite hypothesis: to consider a system as semi-infinite, the region in which diffusion occurs must be significantly smaller than the size of the system; otherwise it must be considered finite, which changes the boundary conditions that apply in the integration of eq. (3) and, thus, the analytical solution to use in the D determination and, hence, the need to know the exact thickness.

Determination of the D of Terphenyl in PS from Local Concentration Profiles

Raman microspectroscopy was applied to establish the local concentration profile of p-terphenyl in the thickness of the PS film. Figure 1 shows the Raman spectra acquired from the surface to the center of the PS film after 72 h of contact with the pellet. The signal of the characteristic peak of p-terphenyl at 1285 cm^{-1} was of high intensity and was well suited to follow the sorption of p-terphenyl. On this basis, four concentration profiles were separately plotted and used to evaluate the D of p-terphenyl with eq. (4). An example of these profiles is plotted in Figure 2. The C/C_∞ ratio was assumed to be represented by the signal ratio A/A_0, where A is the p-terphenyl/PS peak area ratio at each of the points and A_0 is the p-terphenyl/PS peak area ratio at the position $x = 0$. Therefore, no quantification of the concentration was required at this stage for D identification. The average value of D obtained for the four profiles was found to be equal to $2.17 \pm 0.76 \times 10^{-17}$ m^2/s. This proved the a good repeatability of the measure. As shown in Figure 2, p-terphenyl sorption was only detectable in a region as small as 6 μm from the interface of a 260-μm PS film, but this depth was sufficient enough to gain a reliable D value with regard to the Raman microscopy resolution. Also, 6 μm out of 260 μm was in good agreement with the semi-infinite consideration of the system. The same procedure was applied to three other samples after they were in contact for 30 days with the ULMWPE spiked at three different concentration levels (0.5, 2, and 10 wt %). A value of $2.26 \pm 1.13 \times 10^{-17}$ m^2/s was obtained independently of the source content of p-terphenyl on the basis of three concentration profiles taken for each concentration level. This value was not significantly different from the value obtained after 72 h of contact, so a final value of $2.38 \pm 1.08 \times 10^{-17}$ m^2/s was considered. This low D was representative of the slow diffusion process that was to be expected in a high-barrier polymer below its glass-transition temperature.

From a practical point of view, an uncertainty in the interface location during the Raman measurement can be pointed out. To
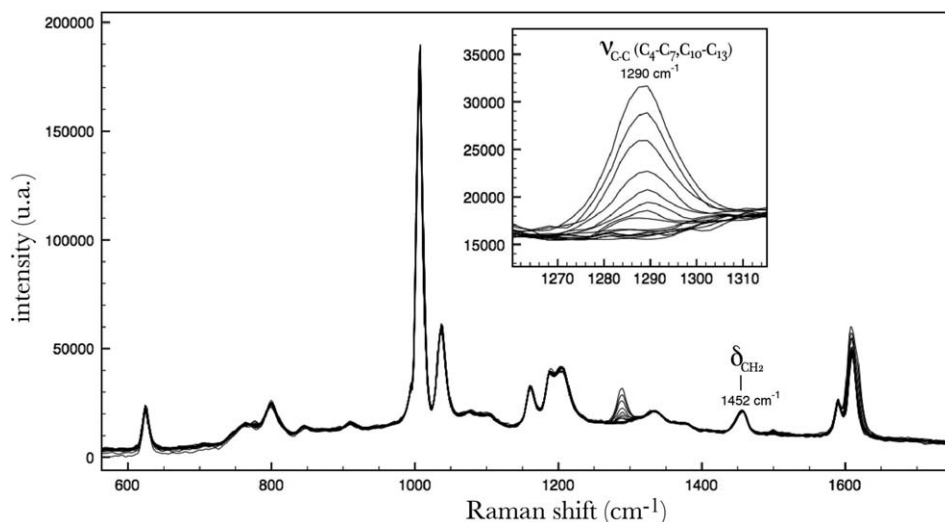
Figure 1. Raman spectral fingerprint of PS + *p*-terphenyl. The focused region shows the peaks selected for following *p*-terphenyl concentration variations in the thickness of the film.

assess the impact of a possible error related to interface location, error propagation during D identification was computed by the introduction of variations within the interval of ± 1 μm in the location of each measurement point. As shown in Figure 3, the sensitivity analysis showed that the D values followed a normal distribution according to the Lilliefors test, with a mean of 2.25×10^{-17} m²/s and a confidence interval of 2.24×10^{-17} to 2.26×10^{-17} m²/s. The mean of the distribution was, consequently, almost exactly the same value as the measured D. The narrow confidence interval indicated that the misplacement of the points did not represent a main source of error in the determination of D.

The determination of D from local concentration profiles obtained with Raman microspectroscopy has already been applied

to low-barrier polymers above their glass-transition temperature. For example, Mauricio-Iglesias et al.[23] reported a D value of 8×10^{-14} m²/s for the optical brightener Uvitex OB (molecular weight = 430.6 g/mol) in linear low-density polyethylene. It was shown in this study that this analytical strategy could also be successfully applied to a high-barrier polymer such as PS below its glass-transition temperature, even if diffusion occurred significantly more slowly.

### Determination of the D of Terphenyl in PS from the Global Concentration Evolution with Time

To clarify the impact of the method of characterization on D, the same system (*p*-terphenyl in amorphous PS at 95°C) was submitted to D determination by global concentration evolution
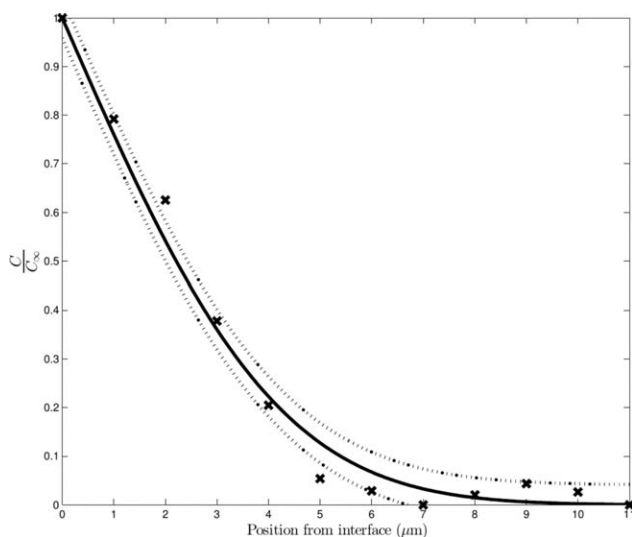
Figure 2. Concentration profile of *p*-terphenyl through the thickness of PS films subjected to contact with a *p*-terphenyl pellet for 72 h. The continuous line represents the profile with the predicted values of D, and the dotted lines represent the predicted concentration ratio plus or minus RMSE, which in this case was 0.0124.
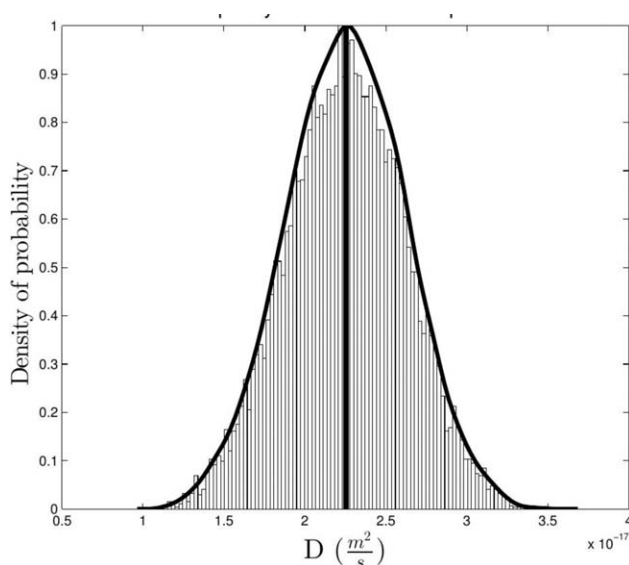

Figure 3. Normal distribution resulting from noise addition within a range of ± 1 μm of the experimental points obtained with Raman spectroscopy. The solid curve represents the modeled normal distribution, and the black vertical line represents the mean of the distribution.
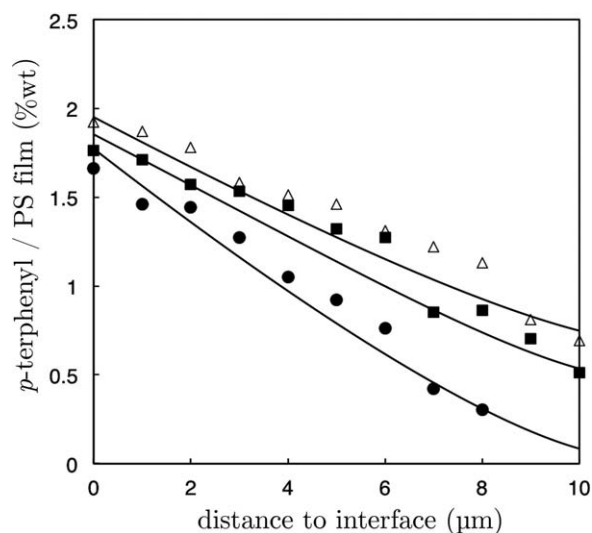
Figure 4. Experimental local concentration profiles (symbols) and predicted local concentration profiles (solid lines) for original PS films resulting from 30 days of contact with ULMWPE spiked with *p*-terphenyl at concentrations of (■) 0.5, (●) 2, and (△) 10 wt %.

Figure 5. Experimental global concentration profile (×) and predicted global concentration profile (line) in a PS film subjected to contact with a ULMWPE source spiked with 0.5 wt % *p*-terphenyl.

measurement with time; this could also be called *kinetics reconstruction* or simply *global measurement*. The classical global concentration approach consisted of the following of the diffusing molecule mass gain in an originally virgin film until equilibrium was reached. As expressed by eq. (5), the knowledge of the value of the concentration at equilibrium, represented by the variable C_∞, is absolutely mandatory. However, according to the value of D obtained previously, equilibrium would be reached after more than 600 years of contact. Because this is unattainable in practice, another way to determine this parameter must be developed; this implies that this technique alone is not sufficient to accurately determine D, at least for slow systems, such as high-barrier polymers such as amorphous PS.

Determination of *p*-Terphenyl Solubility in PS. Because equilibrium in the whole film was unattainable in the period of time of the study, the assumption that the region of the film immediately adjacent to interface reached equilibrium in a reasonable time was made. Raman microscopy was used to measure the local concentration of *p*-terphenyl at the film surface (which was the first point or $x = 0$ in the concentration profile) in contact with the spiked ULMWPE. The PLS regression applied to quantify the concentration of *p*-terphenyl in PS gave a 0.97 regression coefficient for calibration and validation. The RMSE of calibration, which refers to the uncertainty of calibration for the selected data, was 0.246, and the RMSE value for the prediction data was 0.196. These two values attested to the low differences between the nominal concentration and values predicted by the model. The RPD value calculated from the validation data set was 4.8; this could be considered a good indicator of the prediction purpose. With the PLS regression, the sorption of *p*-terphenyl in the thickness of the PS film could be plotted as a function of the concentration (weight percentage). Figure 4 shows examples of the profiles obtained with different source concentrations of 0.5, 2, and 10 wt % after 30 days of
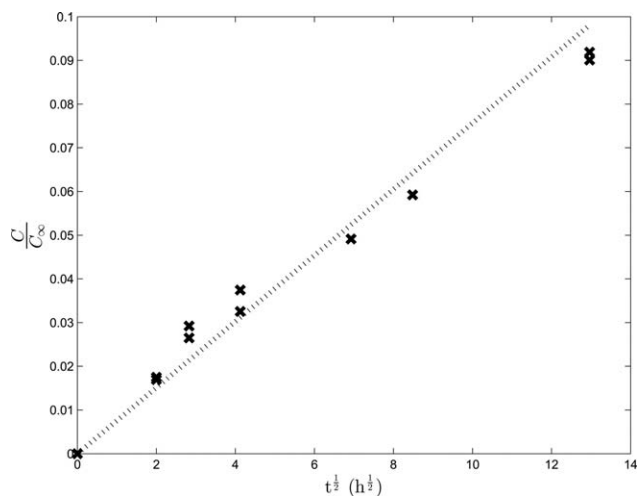
contact. It can be pointed out that the concentration of *p*-terphenyl in PS at the interface, obtained from nine measures with the three different source concentrations, provided a repeatable value of 1.74 ± 0.5 wt %, as shown in Figure 4. This value could be considered as C_∞ of *p*-terphenyl in PS and, consequently, represents C_∞ of the PS after a long time period of contact with the spiked ULMWPE.

Determination of *D*. The sorption kinetics of *p*-terphenyl from ULMWPE to PS were followed by the analysis of the *p*-terphenyl mass uptake by the PS film with GC after extraction. Figure 5 shows the concentration ratio after 1 week of contact. As shown, the representation of the function of the square root of the elapsed time gave a straight line, which clearly indicated a Fickian mechanism of diffusion. However, an extended period of testing of up to 4 weeks resulted in a mild decrease and the stabilization of the *p*-terphenyl content in the PS film, which could be explained by imprecisions in the extraction process that were not correctly represented by the internal standard. The quantification method was developed on the basis of weak concentrations, which were to be expected if the affinity of *p*-terphenyl for PS was low. This affinity turned out to be higher than expected, and consequently, the concentrations found in the actual material lay out of the concentration range for which the quantification method was successfully tested. In addition, the low performance of the extraction (37 ± 4.4%) might have indicated the reprecipitation of *p*-terphenyl, either at the moment of the ethanol addition (reprecipitation along with the PS) or after the reconcentration (solvent volume < C_∞ of *p*-terphenyl). Because of these observations, the methodology was found not to be adapted to amorphous polymers such as PS that cannot support extraction without dissolution (this might cause diffusing molecule losses at the moment of the addition of the reprecipitating solvent) or for volatile compounds that might get lost during solvent purging. Probably because of these issues, the evolution of the measured quantities of *p*-terphenyl as function of time, the sorption phenomena
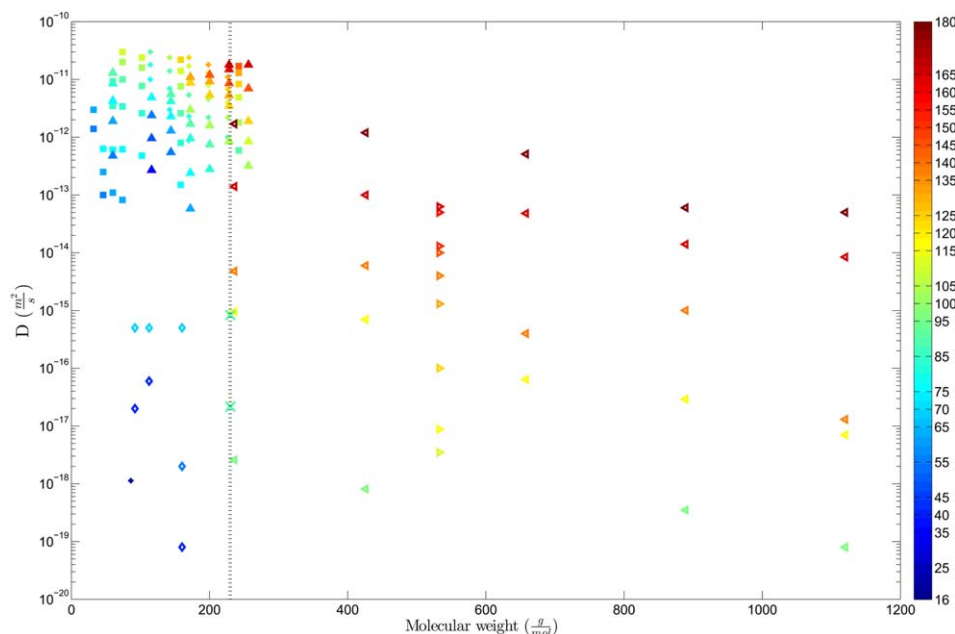
Figure 6. Representation of the dependence of the values of D found in the literature for amorphous PS on the molecular weight and temperature: ($+$) alkanes, gravimetry[13] and spectroscopic ellipsometry;[12] ($\blacksquare$) alcohols, gravimetry;[15] ($\blacktriangle$) carboxylic acids, NMR, and gravimetry;[14] ($\diamond$) toluene, phenyl cyclohexane, and ethyl benzene;[16] ($\blacktriangleleft$) homologous series of fluorescent tracers and FRAP;[17] and ($\blacktriangleright$) rubrene and FRAP.[18] The values obtained for p-terphenyl in this study are represented with $\times$. The dotted line delimits the D values determined by global (left) and local measurements (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

seemed to reach a plateau and was suggested to be close to equilibrium after 1 week of contact.

Taking into account the D value of 2.38×10^{-17} m^2/s previously obtained on the basis of local concentration profiles, the mass of p-terphenyl transferred into the PS film after 1 week of contact reached an estimated value of less than 1.5% of the maximum admissible or equilibrium value. We deducted with the equilibrium value determined with Raman spectroscopy (1.74% of PS) that after 1 week, the concentration of p-terphenyl in the PS film was only 0.025%. Moreover, consideration of the last data point as the equilibrium (as suggested by the pseudo-plateau shape of the curve) would gave D value of an order of magnitude of around 10^{-12} m^2/s, which was more than 10,000 times greater than the value determined from the local concentration profiles. Therefore, to prevent such a huge overestimation of D, attention should be paid to the verification that the last data points describe an effective plateau, indicative of an actual equilibrium state. With Fick's Law for one-sided sorption in a flat film, as represented by eq. (5), with a value of C_∞ of $1.74 \pm 0.5\%$ deduced from the interface concentration with Raman calibration, the fitting of the experimental data produced a D of 89.4×10^{-17} m^2/s. To give an estimation of the extreme importance of the value of C_∞, the latter should have been around 10.5% to obtain a D value of exactly 2.38×10^{-17} m^2/s with the data points obtained with this method; this represents 10 times the value of C_∞ obtained with Raman measurement. As well, an uncertainty propagation analysis performed by the introduction of random variations on C_∞ from within the standard deviation derived from its determination produced a D distribution that

could not be satisfactorily fitted to any known probability distribution, so the 2.5% lower and upper percentiles were removed manually. This corresponded to an interval between 54.5×10^{-17} and 178×10^{-17} m^2/s. The error we obtained from the determination of C_∞ may represent an underestimation or overestimation of D of up to two times its value.

The fact that the value of 89.4×10^{-17} m^2/s found by global measurement was relatively near to the one determined from local concentration profiling (2.38×10^{-17} m^2/s) demonstrated the necessity of using an accurate value of C_∞ in the determination of D by global measurement. In this way, this strategy based on Raman microspectroscopy proved to be more adapted than global measurement for the characterization of both D and the solubility of low-molecular-weight molecules in high-barrier polymers.

Although there were no D values in literature for p-terphenyl in amorphous PS, other molecules with comparable molecular weights at comparable temperatures have been studied. Our bibliographical review, represented in Figure 6 as a function of the molecular weight and temperature, yielded two well differentiated groups of values: the first group, with values in the range 10^{-13} to 10^{-12} m^2/s, were reported for alkanes, alcohols, and carboxylic acids, toluene, phenyl cyclohexane, and ethyl benzene, with concentrations ranging from approximately 30 to 230 g/mol, as measured between 35 to 160°C and determined by the monitoring of the global concentration evolution in time with several analytical techniques, including gravimetry and NMR,[13–15] spectroscopic ellipsometry,[12] and GC–flame ionization detection.[16] It should be pointed that because of the

analytical techniques used by Bernardo and Ogieglo,[12] their data were free from the error source derived from the extraction process described previously. Separately from this first group, the values of a homologous series of fluorescent model molecules[17] and Rubrene, a sensitizer used in chemoluminiscence,[18] whose concentrations ranged from 230 to 1100 g/mol and were measured between 95 and 180°C, had values that went from 10^{-19} to 10^{-12} m^2/s. It is important to point out that this second set of values was determined from the local concentration profiles and more concretely with time-resolved FRAP, which is a technique that is used to follow the diffusion of molecules that exhibit epifluorescence properties. Figure 6 consequently highlights a differentiation in the D values, which appeared to be related to the experimental strategy: local versus global profile. Taking into account the molecular weight of p-terphenyl (230.3 g mol^{-1}) and the temperature at which the experiment was performed (95°C), one might expect a D value in agreement with the first group of values. The significant deviation between the value found in this study and the reported D values measured on molecules of similar molecular weights with global measurement raised a dual issue about the possible overestimation of the Ds determined by the monitoring of the global concentration evolution with time or an underestimation by the methodology based on the concentration profile. Because the data obtained from local measurement contained spatial information in addition to the time information also present in the data obtained by global measurement, the latter was considered to be less precise for D determination. We assumed that the most probable cause of such a difference was the overestimation of the values obtained by the methodologies based on global measurement. Of course, this reasoning was valid if only molecular weight and temperature and not any other physicochemical characteristics of the systems were taken into account as factors influencing diffusion, but nevertheless, it gave us an idea of the kind of imprecision inherent in global measurement when we are dealing with the very slow kinetics that are characteristic of high-barrier polymers.

CONCLUSIONS

Raman vibrational microspectroscopy proved to be accurate for characterizing the D of an additive in a commercial plastic used in the packaging industry from local concentration profiles. This method was originally used for a low-barrier polymer above its glass-transition temperature[23] and was applied here to a high-barrier polymer below its glass-transition temperature with satisfactory results. This methodology was compared with a classical approach consisting of the monitoring of the concentration evolution over time and based on the global measurement of average concentration with GC. The methodology based on local measurement gave a fast, precise, and nondestructive characterization of D. The classic methodology based on global measurement was time consuming, is less precise with consideration of its destructive implementation, requires the extraction of additives from the polymer, and is not especially self-sufficient for very slow kinetics, but it is potentially applicable to any molecule and even to several molecules at once, whereas the methodology based on Raman spectroscopy can only be used in the case of molecules that are detectable with it.

The D values obtained with each methodology, although not identical, were comparable ($2.38 \pm 0.76 \times 10^{-17}$ m^2/s for local measurement and 89.4×10^{-17} m^2/s for global measurement).

Considering the values obtained with diffusing molecules exhibiting similar molecular weights and at comparable temperatures, we observed large difference in D, depending on local or global measurement. The projection of the values obtained in this study showed that D issued from the sorption kinetic integrating reliable estimation of the equilibrium concentration match with the value deducted from local concentration profile. Because a minor underestimation of the value of the equilibrium concentration of the migrant resulted in a large overestimation of D, the implementation of Raman microspectroscopy emerged as an additional useful tool to characterize D and the maximum solubility in high-barrier polymers in the glassy state. The study of other molecules with common structural properties (a homologous series of molecules) on the same polymeric matrix with the same method might allow us to relate differences in the D values with the molecular properties and could be a subject of further research

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