

# Diffusivity of Ethylene and Propylene in Atactic and Isotactic Polypropylene: Morphology Effects and Free-Volume Simulations

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**ABSTRACT:** Diffusion coefficients of propylene and ethylene through particles and films of isotactic polypropylene (iPP) as well as through films of atactic, completely amorphous, polypropylene have been measured by gravimetric experiments. iPP particles with relatively similar crystallinities but with different particle size distributions (PSD), and different origins have been used. They exhibited very different diffusion coefficients when the average radius of the PSD was used as the dimensional parameter of the diffusion process. However, films prepared with these particles and having similar crystallinities provided similar diffusion coefficients. The results are consistent with the idea of a multigrain structure in

the particles, where the apparent (or experimental) diffusion coefficient is a consequence of the complex system formed by internal and external areas. The diffusion coefficient of the films, taken as the real diffusion magnitude, can be used in the calculation of the true diffusional radius of these multigrain particles. Experimental results of the diffusion coefficients have been reasonably well reproduced with the aid of the Vrentas-Duda free volume model. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3871–3878, 2007

**Key words:** poly(propylene); monomer diffusion; Vrentas-Duda model

## INTRODUCTION

Although isotactic polypropylene (iPP) is one of the most important commercial polymers available, in some applications such as automotive components, the pure polymer is too brittle and requires some kind of modification to impart toughness to its relatively brittle character. Ethylene-propylene rubber domains are added to iPP to improve its impact resistance. The final product is denoted as high impact polypropylene (HIPP).<sup>1</sup> This material is usually produced in a hybrid process consisting of propylene polymerization in the liquid phase followed by copolymerization of ethylene and propylene in the gas phase.

In preparing particles of HIPP, ethylene and propylene monomers should diffuse through previously obtained iPP particles. The copolymerization takes place at temperatures in the interval 310–350 K and in a pressure range between 1.5 and 3 MPa. It is clear that properties, such as solubility and diffusivity of monomer, in the polymer are important in

modeling such type of processes. Although the available experimental methods seem to be well founded, the complexity of the polyolefin particles (specially in terms of porosity, size distribution, crystallinity, and crystalline morphology) has given rise to some unsolved problems.

In the experimental determination of the diffusion coefficients, the second Fick's law is the usual equation to reduce the experimental data. But the application of this equation requires the knowledge of the geometric shape of the sample (flat films, spheres, cylindrical bars, etc.) and their characteristic dimensions. In the case of the iPP particles, it could be assumed that they are spherical, an assumption that, in some cases, TEM micrographs support.<sup>2</sup> But TEM micrographs also clearly show that these particles have a complex structure. They can be seen as aggregates of smaller particles, generated as a consequence of the presence of different catalyst points, with important pores among them. In fact, Floyd et al.<sup>3</sup> proposed some years ago a model for propylene and ethylene polymerizations in which they took into account such type of structure. Consequently, the average radius of the whole particle does not represent the true diffusional dimension of the process and, if it is used to calculate diffusion coefficients, these should depend on the particle size distribution (PSD) and the internal morphology of the sample.

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In this article, we have used iPP particles with different morphologies and different PSD. We have confirmed that the diffusion coefficient is not characteristic of the polymer but depends on the particle size if the average radius is used as characteristic dimension of the material. We have hypothesized that polymer films with controlled thickness, obtained after melting the particles, have a well-defined geometry that can provide reliable diffusion coefficients. With these diffusion coefficients of the films, the apparent values obtained with the particles can be used to calculate the true diffusional radius of each type of particles, giving an idea of the multigrain characteristics of the particles in a specific sample.

Our experimental results of diffusion coefficients on film samples have been compared with simulated diffusion coefficients obtained using the so-called Vrentas and Duda<sup>4</sup> model. Although this free-volume model has repeatedly shown its capacity to reproduce experimental results, it requires an important number of parameters, characteristic of the polymer and the penetrant. Fortunately, in the PP case, all these parameters, except one that remains as adjustable, have been recently obtained, as we will detail in the next paragraphs.

The results here summarized are not only important for understanding and modeling the diffusion process during the HIPP polymerization reaction but also in the design of monomer removal equipments, where after the production of polymer particles in slurry or gas-phase reactors, significant amounts of the monomers or comonomers must be removed to meet quality, safety, and environmental standards.

## EXPERIMENTAL PART

### Materials

Table I summarizes the different investigated samples. H-171-II is a REPSOL-YPF (Mostoles, Madrid, Spain) sample of iPP. Received in form of particles, its molecular weight averages by SEC were  $M_n = 71,800$  and  $M_w = 244,700$ . Crystallinity was 36% (as raw particles, determined by DSC on the basis of

a heat of melting of 190 J/g for a 100% crystalline iPP). Fractions of particles with different PSDs were obtained by screening using testing sieves. Only the two extreme fractions have been used in this article, as Table I indicates. Crystallinities of these fractions, following the procedure earlier described, were in the 35–39% interval.

Films of these particles were prepared after melting them at 200°C and keeping this temperature for two minutes. The melt was then transferred to another unit at room temperature to allow crystallization.

Using the same protocol, a different film was prepared from a randomly selected sample (in pellet form) of another REPSOL-YPF iPP (the one called PP 070) to compare results from different films of commercial iPPs. According to the supplier, isotacticity was 95% and the viscosity-average molecular weight  $\bar{M}_v$  was 164,700.

The atactic polypropylene (aPP) was also supplied by REPSOL-YPF and denoted as aPP141. It was obtained by polymerization in heterogeneous phase using metallocenic catalysts. It is a rubbery material with a glass transition near 280 K. The molecular weight distribution was characterized by SEC in chloroform at 25°C. The weight average molecular weight was 70,000 and the polydispersity 2.2. <sup>13</sup>C-NMR in 1,2,4-trichlorobenzene/deuterated benzene gives the following dyad analysis: (mm) = 14.1%; (rm) = 50.7%, and (rr) = 35.2%. The film was prepared by molding the sample at room temperature. Because of the rubbery character and to prevent some undesirable flow during the gravimetric experiments, the aPP film was thicker than the iPP ones.

Finally, we have investigated iPP particles provided by SABIC (Geleen, Holland). The weight average molecular weight was 395,000 and the number average molecular weight 80,000, as reported by the supplier. Another film was prepared with these particles following the earlier described methodology.

Ethylene (>99%) and propylene (>99%) were provided by Air Liquide in the form of gas cylinders. They were used as received. Propylene was in the form of a pressurized liquid in equilibrium with its vapor. Given that the cylinder was maintained at

TABLE I  
Characteristics of the Different Samples of Polypropylene Used in the Gravimetric Experiments

Polymer	Supplier	Cryst. (%)	Morphology	Characteristic dimensions: average diameter $\phi$ , thickness $\ell$ (mm)
iPP H-171-II	REPSOL-YPF	36	Original particles	$\phi = 1800$
iPP H-171-II	REPSOL-YPF	39	Particles after fractionation	$\phi = 2900$
iPP H-171-II	REPSOL-YPF	35	Particles after fractionation	$\phi = 900$
iPP H-171-II	REPSOL-YPF	44	Film	$\ell = 562$
iPP PP 070	REPSOL-YPF	40	Film	$\ell = 204$
aPP aPP 141	REPSOL-YPF	0	Film	$\ell = 701$
iPP	SABIC	33	Original Particles	$\phi = 693$
iPP	SABIC	51	Film	$\ell = 224$

room temperature, it was not possible to perform gravimetric experiments at pressures above the vapor pressure of propylene in these conditions.

The required thickness of the different films ( $\ell$ ) was measured by a Duo Check gauge with an accuracy of 1  $\mu\text{m}$ . In the case of the particles, the average radius was calculated assuming a spherical morphology and taking as average volume of the particles the maximum in the PSD. PSDs of the original samples were provided by the suppliers.

### Sorption experiments: Data reduction

Gravimetric sorption experiments have been carried out in an electromagnetic balance sold under the trade name of IGA-2 by Hiden in United Kingdom. It operates with gases and vapors in a wide range of temperatures and up to 20 bars.<sup>5</sup> It can be programmed both in sorption and desorption experiments, where the pressure is increased or decreased in a step-by-step mode. We have performed experiments at different temperatures. 60°C and 80°C were selected because they are close to the interval used in the HIPP polymerization. But these temperatures are far from the aPP glass transition temperature, making difficult to keep the dimensional stability of its films. Because of that, sorption experiments in the vicinity of 30° and 40° were carried out with the aPP film, as well as some iPP particles and films provided by REPSOL-YPF (see next paragraphs). At these temperatures, aPP and the iPP amorphous regions are above the glass transition temperature and, consequently, in a rubbery state.

During the gravimetric experiments, the weight gain ( $M_t$ ) increases with time ( $t$ ) up to an equilibrium value,  $M_\infty$ . The Avrami's semiempirical model, originally developed to explain the kinetics of metal crystallization, can be used to describe the sorption kinetics of a penetrant in a polymer, according to eq. (1):

$$M_t = M_\infty [1 - \exp(-(t - t_0)^x / \kappa)] \quad (1)$$

where  $x$  is an exponent allowing the fitting of non-fickian curves,  $\kappa$  is a time constant related with the diffusional process and  $t_0$  is the actual origin from which the trend is analyzed, after eliminating some weight readings affected by aerodynamic disturbances occurring during the pressurization of the balance. All our sorption kinetics had an approximately fickian behavior ( $x = 1$ ). This simplifies eq. (1).

It is possible to demonstrate that this equation can be derived from the so-called long-time approximation of the general equation:<sup>6</sup>

$$\frac{M_t}{M_\infty} = 1 - \frac{A}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{x^2}\right) \quad (2)$$

obtained by solving the differential equation corresponding to the second Fick's law. The  $A$  constant equals to 8 and  $x = \ell$ , where  $\ell$  is the thickness, in the case of a sample of rectangular geometry. In the case of spherical particles  $A = 6$  and  $x = r$ , where  $r$  is the average radius of the particle.

In our case, diffusivities have been calculated from the time constant  $\kappa$  provided by a least squares analysis of the experimental data, using eq. (1). In the particle case and assuming a spherical geometry,<sup>6</sup>  $\kappa$  and  $D$  are related by:

$$D = \frac{1}{\kappa} \frac{r^2}{\pi^2} \quad (3)$$

If the sample is in the form of a film with rectangular geometry and a thickness  $\ell$ ,

$$D = \frac{1}{\kappa} \frac{\ell^2}{\pi^2} \quad (4)$$

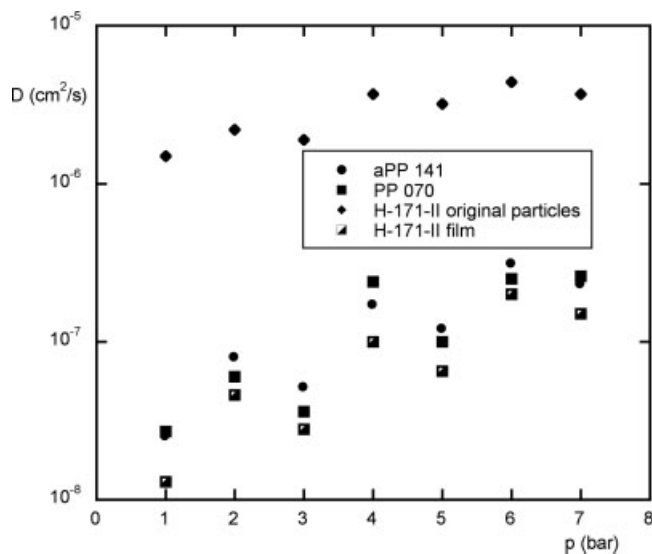
## RESULTS AND DISCUSSION

### Experimental diffusion coefficients

As previously mentioned, iPP particles are aggregates of smaller particles with extended pores among them.<sup>2</sup> These pores are completely accessible to the penetrant, and consequently, the use of the average radius of the aggregate as representative diffusivity path of the process could introduce some uncertainty in the determination of the real diffusion coefficient. Our hypothesis was that the best way to determine this diffusion coefficient ( $D$ ) is to use dense films of the different samples. In using films, we have bulk samples with a completely controlled geometry. The thickness, which is the dimensional value appearing in eq. (4), can be measured with high accuracy ( $\pm 1 \mu\text{m}$ ). If the hypothesis is correct, we have to find similar diffusion coefficient with films prepared with different iPP samples. The only condition is that the crystallinity degree should be similar.

This final condition arises from the fact that it is generally accepted that the penetration of small-molecule penetrants in semicrystalline polymers is restricted to the noncrystalline fraction. Consequently, because of the presence of the crystallites, the trajectory of the penetrant molecule is extended with respect to that in the fully amorphous or rubbery polymer. This extension is usually quantified in terms of a geometrical impedance or tortuosity factor.<sup>7</sup>

On the other side, if our hypothesis is correct, the diffusion coefficients obtained using films would differ from those of the particle samples, in which the use of the average radius should lead to apparent



**Figure 1** Diffusion coefficients of propylene (40°C) in different REPSOL-YPF samples.

diffusion coefficients, depending on the PSD and the particle morphology.

Figure 1 summarizes diffusion coefficients of propylene at 40°C in films and particles of different REPSOL-YPF samples. It shows that the particles as received from the supplier have a significantly higher diffusion coefficient than those of the films. This result confirms our original hypothesis, according to which, this would be the consequence of using the average radius as characteristic dimension of the particles to calculate  $D$ . The diffusion coefficient of the particles so calculated is, in average, 50 times higher than  $D$  of the corresponding film. Taking into account that the radius appears in eq. (3) as a square, this would imply that the effective diffusion radius is seven times smaller than the average one.

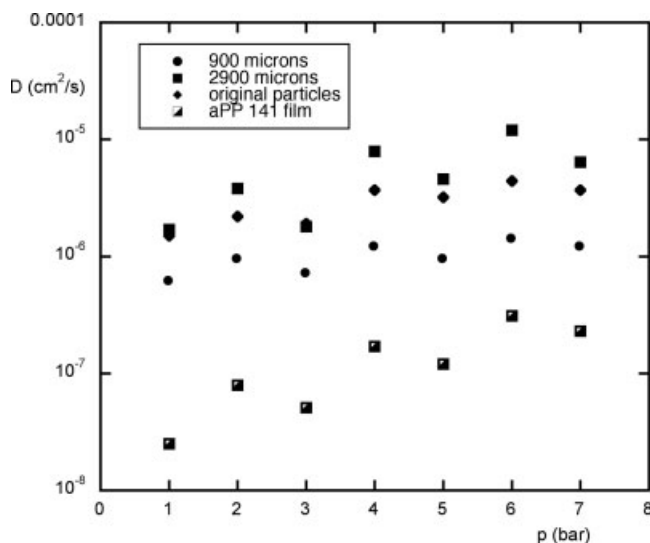
The second interesting but intriguing result in Figure 1 is that the two films of iPP and the film of aPP exhibit similar diffusion coefficients. Although in the case of the two iPP films the result could be understood in terms of their similar geometries and crystallinities, the case of aPP is certainly surprising if we consider the usual concepts<sup>7</sup> about the tortuosity induced by the crystalline regions.

In the experimental section we have described the difficulties in performing sorption experiments with aPP at 40°C. The whole sample is above its  $T_g$  and, eventually, it can flow during the gravimetric experiment, changing the original thickness, as a visual inspection at the end of the tests has revealed. However, no special changes were observed in the sorption profiles of the different experiments. The thickness changes during the experiments do not seem to be in the origin of the similar diffusion coefficients observed with the iPP and aPP samples: when the aPP film reduces its thickness during the experiment the corre-

sponding diffusion coefficient should be overestimated, leading to actual  $D$  values lower than the ones of the crystalline samples, a result difficult to explain.

It is also true that, for the reasons explained in the experimental part, the aPP film was thicker than the iPP films. This is important because in calculating  $D$  using the equations of the precedent sections, it is implicitly assumed that the thickness dimension is negligible with respect to the other two dimensions of the film. When the sample is progressively thicker, its specific surface decreases and the diffusion process slows. For instance, when the thickness increases one order of magnitude (100  $\mu\text{m}$ –1 mm) the specific surface of a rectangular sample decreases in a factor between two and three. This will be in the origin of a  $D$  value of aPP lower than expected and similar to the  $D$  values of the iPPs. In fact, the differences between the two iPPs could be caused, in part, by the different thickness of the two samples.

The effect of the particle size (and of the average radius used in calculating  $D$ ) is more clearly evidenced in Figure 2. Here, we are including diffusion coefficients (at 40°C) of the original particles and those of two fractions of particles having the extreme particle average radii of the original PSD, from which they were obtained. In comparing the diffusion coefficients of these two fractions, the smallest particles exhibit a lower diffusion coefficient. This is consistent with our hypothesis. When the particles are becoming smaller, the aggregation is less important and the average radius tends to the true diffusional dimension. Even in the case of these small particles, there are differences of about a factor of 10 between the experimental  $D$  results and the values of the atactic PP (selected as a reference, given the similarities between its diffusion coefficient and



**Figure 2** Diffusion coefficient of propylene (40°C) in REPSOL-YPF particles of different sizes.

those of the films included in Fig. 1). This would imply that, in the case of the smallest particles, the effective diffusion radius is about 3 times the average one. A similar situation has been found at 60°C.

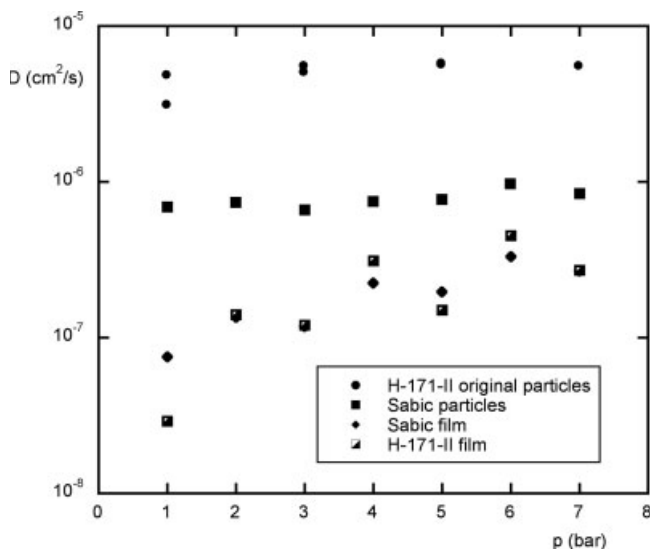
An interesting result, which confirms the dependence of the diffusion coefficient on the average radius used in calculating  $D$ , is summarized in Figure 3. Particles provided by SABIC are smaller (693  $\mu\text{m}$  as average diameter) than the REPSOL-YPF ones (1800  $\mu\text{m}$ ). Consequently, the diffusion coefficients calculated with these dimensions are different and smaller in the case of the small particles. However, the diffusion coefficients in the films prepared with these particles are in reasonable agreement (they have similar crystallinity degrees). These films have  $D$  coefficients smaller than those of their corresponding particles.

Similar results have been obtained in the case of ethylene. As an example, Figure 4 shows results at 60°C with the H-171-II REPSOL-YPF original particles and the film prepared with them. A close comparison of Figures 3 and 4 clearly shows that the difference between the diffusion coefficient of the particles and films is higher in the case of the propylene penetrant. This could be related with the different size of the penetrant molecules and/or with the higher propylene activities used in the experiments.

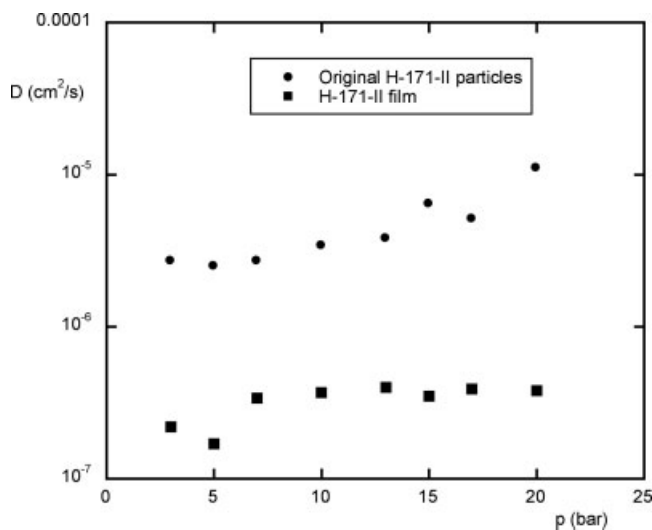
Finally, Table II summarizes the average diffusion coefficients of ethylene and propylene at the three investigated temperatures. These averages were calculated using all the investigated films.

### Theoretical approach to the experimental diffusion coefficients

As a final conclusion of the previous section, the true diffusion coefficients of ethylene and propylene



**Figure 3** Diffusion coefficient of propylene (60°C) in REPSOL-YPF and SABIC particles and in the films prepared with them.



**Figure 4** Diffusion coefficient of ethylene (60°C) in REPSOL-YPF particles and in the films prepared with them. Note that with this penetrant pressure goes up to 20 bars.

through the iPP particles and films are those obtained using films with a well-known geometry and a measurable thickness. As an additional test of the validity of this conclusion, we have calculated diffusion coefficients with the aid of one of the models that has been proposed for describing diffusion of low molecular weight gases or vapors in amorphous polymers above the glass transition.

The most successful models for describing the diffusional process are based on free volume concepts in which the components of the system are envisioned to migrate by jumping into the free-volume holes formed by natural thermal fluctuations. These basic free-volume concepts were first proposed by Cohen and Turnbull,<sup>8</sup> modified by Fujita<sup>9</sup> for the case of diffusion in amorphous, rubbery polymers and refined by Vrentas and Duda<sup>10,11</sup> for both self and mutual diffusion in polymer-solvent systems.

According to Vrentas and Duda the diffusion of a penetrant will depend on the probability to create a hole sufficiently big near of the penetrant molecule and on the probability that this molecule gets energy enough to jump into the hole. The basic assumptions made in that model:

**TABLE II**  
Average Values of Propylene and Ethylene Diffusion Coefficients at the Three Investigated Temperatures. All the Samples were Tested in the Film Morphology

	$D_{40} \times 10^7$ ( $\text{cm}^2/\text{s}$ )	$D_{60} \times 10^7$ ( $\text{cm}^2/\text{s}$ )	$D_{80} \times 10^7$ ( $\text{cm}^2/\text{s}$ )
Propylene	0.9 ( $\pm 0.2$ )	1.8 ( $\pm 1.0$ )	3.5 ( $\pm 1.1$ )
Ethylene	2.9 ( $\pm 1.0$ )	3.0 ( $\pm 1.0$ )	6.7 ( $\pm 2.1$ )

- Thermal expansion coefficients necessary to calculate different volumes are considered not to change in the temperature range of work.
- The partial specific volumes of the solvent and polymer are considered to remain constant at different concentrations.
- The chemical potential of the solvent is calculated by the Flory–Huggins equation, where the polymer/solvent interaction parameter will be constant at different concentrations and temperatures.

The original formulation has had several modifications to be adapted to different systems.<sup>12,13</sup> Although, the original model is not totally predictive, the authors have recently proposed<sup>14</sup> the possibility of obtaining all the parameters without using experimental data of diffusion coefficients.

In this theory the self-diffusion coefficient for the solvent is calculated as:

$$D_1 = D_0 \exp\left(\frac{-E^*}{RT}\right) \exp\left(\frac{-(w_1 \hat{V}_1^* + \xi w_2 \hat{V}_2^*)}{\hat{V}_{FH}/\gamma}\right) \quad (5)$$

where  $D_0$  is a preexponential factor,  $E^*$  the activation energy required for a molecule to overcome the attractive forces holding it to its neighbors,  $\hat{V}_i^*$  is the critical local hole free volume required for a  $i$  unit to jump,  $w_i$  is the weight fraction of  $i$  component, and  $\gamma$  is an overlap factor (between 1/2 and 1) introduced to correct for overlapping free volume. The  $\xi$  parameter is the ratio of polymer and solvent molar jumping units, defined by the following equation:

$$\xi = \frac{\hat{V}_1^0(0)}{\hat{V}_{2j}^*} = \frac{M_{j1} \hat{V}_1^*}{M_{j2} \hat{V}_2^*} \quad (6)$$

where  $M_{ji}$  is the molecular weight of a jumping unit of component  $i$ .

Finally,  $\hat{V}_{FH}$  is the critical free volume of the system and is calculated by:

$$\frac{\hat{V}_{FH}}{\gamma} = w_1 \frac{k_{11}}{\gamma_1} (k_{21} - T_{g1} + T) + w_2 \frac{k_{12}}{\gamma_2} (k_{22} - T_{g2} + T) \quad (7)$$

where  $k_{1i}$  and  $k_{2i}$  are free volume parameters, with dimensions of temperature, that can be calculated using viscosity-temperature data of the component and the Vogel empirical equation adapted to the Vrentas and Duda nomenclature.<sup>15</sup>

The critical volumes  $\hat{V}_i^*$  can be estimated from group contribution correlations.  $D_0$ ,  $\frac{k_{11}}{\gamma}$ , and  $k_{21} - T_{g1}$  can be determined by correlating viscosity and specific volumes of the penetrant at different temperatures.  $\frac{k_{21}}{\gamma}$  and  $k_{22} - T_{g2}$  can be adjusted using viscosity-temperature data of the polymer.

Using the Flory–Huggins theory, the self diffusion coefficient of the solvent ( $D_1$ ) can be related to the

binary mutual diffusion coefficient ( $D$ ) as:

$$D = D_1(1 - \phi_1)^2(1 - 2\chi\phi_1) \quad (8)$$

where  $\chi$  is the Flory–Huggins interaction parameter that accounts for the influence of the polymer/penetrant interactions in the diffusion process.  $\phi_1$  is the penetrant volume fraction. These data are accessible from our sorption experiments given that  $M_\infty$  in eq. (1) is the equilibrium penetrant mass absorbed in the polymer mass originally hanged in the balance. With these two masses and the densities of the polymer and the penetrant,  $\phi_1$  can be easily calculated. In the case of the polymer, we have used the density of the amorphous polymer<sup>16</sup> assuming that only these regions are available to the penetrant.

The interaction parameter,  $\chi$ , can be calculated with the aid of the Flory–Huggins expression:

$$\ln a_1 = \ln \phi_1(1 - \phi_1) + \chi(1 - \phi_1)^2 \quad (9)$$

where the activity of the penetrant is calculated by,

$$a_1 = \frac{p_1}{p_1^0} \quad (10)$$

using the vapor pressure of the pure penetrant at the experimental temperature and the vapor pressure of the penetrant in equilibrium with the solution obtained during the gravimetric sorptions.

Consequently, the parameters we need for calculating  $D_1$  are:  $D_0$ ,  $E^*$ ,  $\hat{V}_i^*$ ,  $\xi$ ,  $k_{11}/\gamma$ ,  $k_{21}$ ,  $T_{g1}$ ,  $k_{21}/\gamma$ ,  $k_{22}$ , and  $T_{g2}$ . Fortunately, the majority of these parameters have been reported in different papers of the authors of the model and are resumed in the following Tables III and IV. The critical volumes  $\hat{V}_i^*$  can be estimated from group contribution correlations.  $\xi$  has been calculated using eq. (6) and a correlation given by Hong<sup>17</sup> for calculating  $\hat{V}_{2j}^*$  in amorphous polymers above the glass transition temperature:

$$\hat{V}_{2j}^*(\text{cm}^3/\text{mol}) = 0.0925 \times T_{g2}(\text{K}) + 69.47 \quad (11)$$

Using for  $T_{g2}(\text{K})$  a value of 253, as resumed in Table I,  $\hat{V}_{2j}^* = 92.87$  and the corresponding values for  $\xi$  are:

$$\begin{aligned} \xi(\text{PP/propylene}) &= 0.554 \\ \xi(\text{PP/ethylene}) &= 0.404 \end{aligned}$$

Figure 5 summarizes experimental results of Flory–Huggins interaction parameters of propylene

**TABLE III**  
Free-Volume Parameters for Atactic Polypropylene as given by Vrentas and Duda<sup>11</sup>

$\hat{V}_2^*(\text{cm}^3/\text{g})$	$(K_{12}/\gamma) \times 10^4(\text{cm}^3/\text{gK})$	$K_{22}-T_{g2}(\text{K})$	$T_{g2}(\text{K})$
1.005	5.02	-205	253

TABLE IV  
Free-Volume Parameters for Propylene and Ethylene as given by Palamara<sup>16</sup>

	$\hat{V}_1^*$ (cm <sup>3</sup> /g)	$(K_{11}/\gamma) \times 10^3$ (cm <sup>3</sup> /gK)	$K_{21}-T_{g1}$ (K)	$D_0$ (cm <sup>2</sup> /s)
Propylene	1.225	2.91	-8.657	$7.65 \times 10^{-2}$
Ethylene	1.341	1.97	42.38	$2.96 \times 10^{-3}$

and ethylene at 40°C in aPP, an additional parameter necessary for the model calculations. In the propylene case, an average value of 0.55 seems representative. However, in the next paragraphs, we will show that, in the concentration range we are involved, the value of the interaction parameter is irrelevant in the calculation of the  $D$  coefficient.

Consequently the only adjustable parameter is  $E^*$ . To adjust its value, Figure 6 contains experimental data of different aPP films at 303 and 310 K as well as the best fitting using an  $E^*$  value of 3800 cal/mol. This value is not very different from the 3210 value used by Palamara.<sup>18</sup>

Using all the required parameters, the self-diffusion coefficient  $D_1$  can be calculated using eq. (5). With these values, using eq. (8) and the interaction parameters calculated from solubility data, the mutual binary diffusion coefficient can be estimated as a function of the weight fraction of the penetrant in the polymer. This weight fraction has been calculated on an amorphous basis.

Figure 7 shows the results of this type of calculation for propylene. As expected, according to eq. (8), both coefficients ( $D_1$  and  $D$ ) are similar at low penetrant concentrations, whereas at higher concentration, the term containing the interaction parameter in this equation has a more pronounced effect in its evolution with the penetrant concentration. Given the limited solubilities of the two penetrants, our experimental

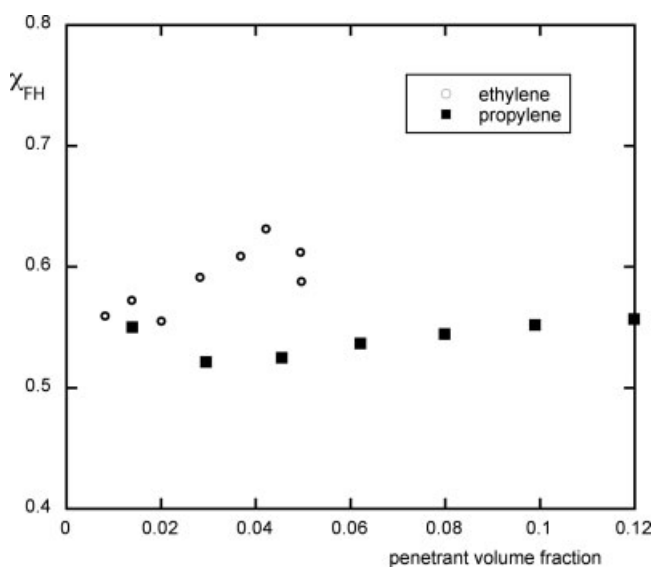


Figure 5 Flory-Huggins interaction parameters at 40° for ethylene and propylene in atactic polypropylene.

results are in a restricted interval of concentrations where the value of the interaction does not affect the calculation of the mutual binary diffusion coefficients.

Figure 8 contains a comparison between experimental and calculated diffusion coefficients of propylene in polypropylene at 333 K. In this figure, the experimental data correspond to the two different iPP samples provided by Repsol.

Diffusion coefficients of ethylene in polypropylene have been similarly reproduced (Fig. 9) with an  $E^*$  value of 2300 cal/mol and without considering the effect of the term containing the interaction parameter, given that the concentration of the penetrant is even lower than in the case of propylene.

## CONCLUSIONS

Gravimetric sorption experiments are reliable, relatively nontime consuming methods for a simultaneous determination of the solubility and the diffusivity of gases and vapors in polymers. In this article, gravimetric experiments have been used to study the diffusivities of ethylene and propylene monomers through previously prepared particles of iPP.

However, in calculating diffusion coefficients using this technique with iPP particles, the average particle radius of the polymer is not the correct diffusional dimension. The bigger is the particle, the

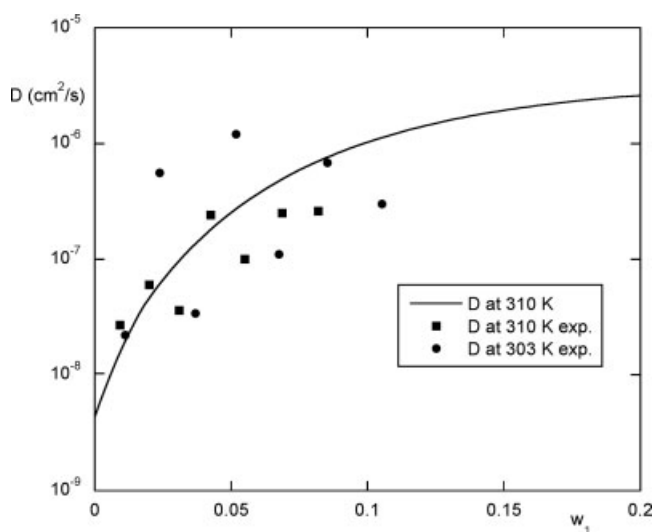
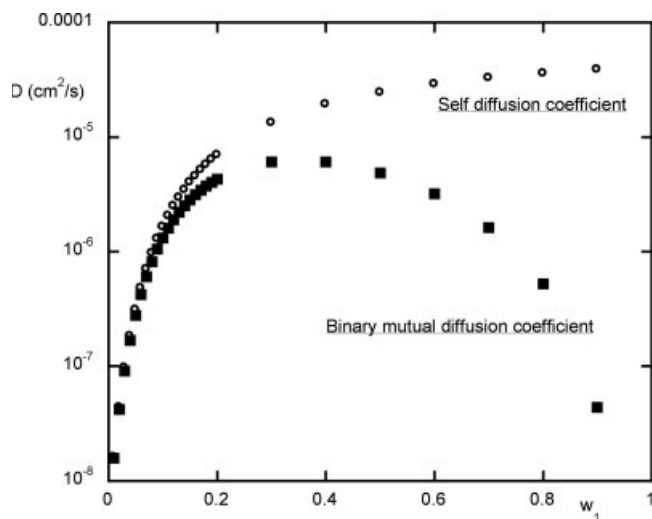


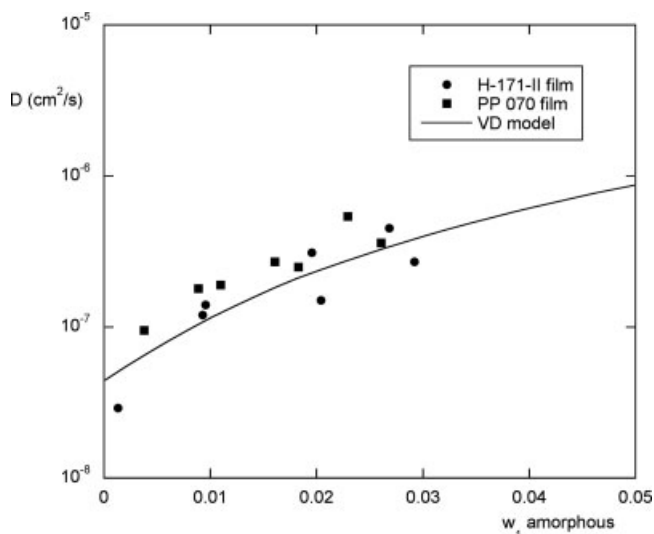
Figure 6 Adjusting the  $E^*$  parameter (3800 cal/mol) using experimental propylene  $D$  data through atactic PP at two temperatures.



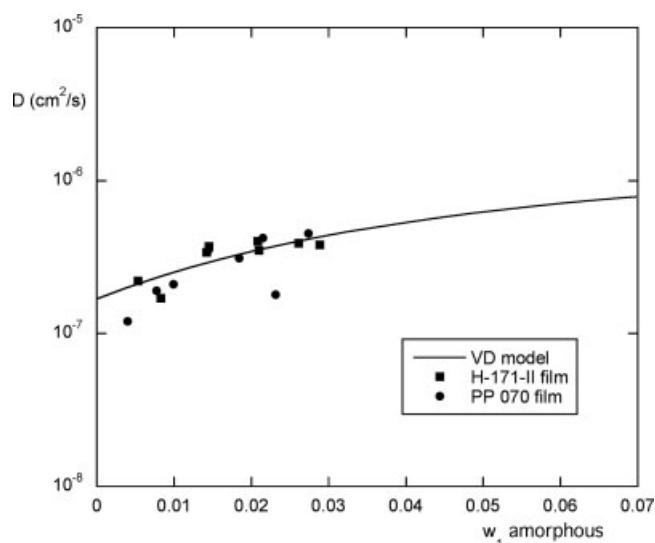
**Figure 7** The self and the mutual binary diffusion coefficients at 310 K as a function of the weight fraction of propylene in atactic polypropylene.

higher is the apparent diffusion coefficient. This seems to be a consequence of the multi-grain structure of the particles. Effective diffusion radius of these particles can only be calculated after knowing the diffusion coefficient obtained with films of well-characterized thickness. Using this morphology, similar diffusion coefficients are obtained with samples provided by two different suppliers.

Diffusion coefficients can be reasonably reproduced with the aid of the Vrentas-Duda model. Although the model requires an important number of parameters they are known in the case of the systems considered in this article.



**Figure 8** Experimental and calculated (Vrentas-Duda model) diffusion coefficients of propylene in isotactic polypropylene at 60°C.



**Figure 9** Experimental and calculated (Vrentas-Duda model) diffusion coefficients of ethylene in isotactic polypropylene at 60°C.

The experimental and theoretical results here summarized may be of interest in understanding the processes involved in the preparation of High Impact Poly (propylene) (HIPP) particles.

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