

# Water Diffusion into Transcrystalline Layers on Polypropylene

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**ABSTRACT:** The diffusion constant of water through transcrystalline surface layers on isotactic polypropylene (i-PP) is reported. A suitable experimental technique was developed, based on sorption or desorption measurements. The accompanying change in sample weight is detected by the corresponding change in mechanical resonance frequency. The facility allows investigation of the diffusion current parallel to as well as perpendicular to the sample surface. Tests with commercial polyethylene films revealed that reproducibility and reliability are better than 6%. The samples were prepared as thin films in which the transcrystallinity was controlled by use of several substrate materials and different thermal conditions during solidification of the melt. The water diffusion constant of finely spherulitic i-PP turned out to be  $15.9 \mu\text{m}^2/\text{s}$ ; whereas the values for transcrystalline material amounted to  $19.6 \mu\text{m}^2/\text{s}$  parallel and between 12 and  $10 \mu\text{m}^2/\text{s}$  perpendicular to the film surface, depending on the actual supermolecular structure. These results are discussed with respect to the underlying transcrystalline texture and the texture of the amorphous percolation network. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3275–3285, 1999

**Key words:** diffusion coefficient; diffusion measurement; water diffusion; transcrystallinity; isotactic polypropylene

## INTRODUCTION

The structure at the surface of a material must differ from that of the bulk for a number of reasons. Solidification starts at the surface where the cooling surroundings acts. A temperature gradient develops then, which, in crystallizable materials, causes the number density of growing crystalline entities in the vicinity of the surface to be much larger than in the bulk. Second, the surface of the melt container occasionally has a much

stronger nucleating efficiency than those heterogeneities within the material which usually nucleate crystallization. Sometimes, this activity may be so strong that epitaxy occurs as follows: the size of a critical nucleus becomes smaller than a crystalline atomic layer, and the primary nucleation step is replaced by secondary nucleation, that is, immediate growth. Due to spatial restrictions, the huge number of surface nucleated crystalline entities can then grow only in one or two directions. This results in a textured morphology with the texture axis and the growing direction pointing perpendicularly from the surface into the interior. Finally, when solidification is accompanied by motion of the melt as during extrusion or when filling a tool during injection molding, an inhomogeneous shear rate distribution results, leading to an inhomogeneous chain orientation distribution. Both, in their turn, are most distinct

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in the vicinity of the tool wall, where, consequently, nucleation density and texture are accordingly pronounced. The resulting surface layers are called transcrystalline.

All these features are particularly pronounced in polymers.<sup>1-3</sup> Compared to many other materials, plastics have a rather low thermal conductivity. Huge temperature gradients can therefore develop at the container/plastic material interface, amounting<sup>4,5</sup> to up to 100 K/mm and being stable for most of the crystallization time. Due to the low heat conductivity, polymers can be heavily undercooled such that nucleation phenomena play an important role. Finally, since being viscoelastic, plastics develop distinct shear rate distributions when filling a form. The thicknesses of the resulting transcrystalline surface layers vary between several micrometer up to several millimeters, depending on the actual conditions. Its structural features, like crystallinity, texture, or spherulite number and size, differ remarkably from those of the bulk. They change gradually with increasing distance from the surface and finally approach those of the bulk.

Consequently, transcrystallinity is a well-known phenomenon in plastics processing.<sup>1-3</sup> This structural feature rules a large number of material properties that are determined by the structure at the surface. Examples may be all optical properties like reflectivity, color, brilliance, or transparency. Mechanical hardness is mainly determined by the surface structure too. Electrical properties like surface resistance and electrostatic charging also depend on the structure at the materials surface. Finally, corrosion starts there. In many cases, the extent of the latter depends on the rate by which environmental influences can spread through the material. This, in turn, depends on the rate of diffusion of agents through the surface, on its permeability, and on its sorption ability. If the surface is a barrier layer, the whole material is protected.

We report here on the diffusion constant  $D$  of water through transcrystalline layers on isotactic polypropylene (PP) as grown on different substrate materials like several metals (aluminum, copper, and steel) and polymers such as polyethylene terephthalate (PET), polyimide (PI), and polytetrafluoroethylene (PTFE). Glass was included into the investigations too. Such information may be interesting for food packaging and in electrical insulation and for other applications.<sup>6</sup>

There is only rare information on water diffusion through polypropylene in the literature so far

and that information contradicting where available.<sup>6-12</sup> Jeschke and Stuart<sup>7</sup> gives  $D = 24 \mu\text{m}^2/\text{s}$ , which is found by a gravimetric technique for PP with a density of  $0.907 \text{ g/cm}^3$ . This value was confirmed ( $D = 20 \mu\text{m}^2/\text{s}$ ) by Yasuda and Stannett.<sup>8</sup> McKnight and Gillespie Jr.<sup>9</sup> reports on the temperature dependence of  $D$  as determined by infrared (IR) absorption and found  $D = 3.8 \mu\text{m}^2/\text{s}$  at ambient temperature. Although it is acknowledged that the diffusion ability depends sensitively on the existence of additives or other impurities in the material, on environmental influences, which may change the chemistry of the material, and on the actual crystalline and supermolecular structure, usually no detailed information on these features is given. We will pay particular attention here to the anisotropic diffusion behavior of transcrystalline layers perpendicularly and parallel to the surface, that is, to the role of the texture of the material under investigation.

A suitable technique had been developed and reported on previously.<sup>13,14</sup> It uses the thickness measuring facility for deposited layers on samples for electron microscopy. The experimental procedure includes several crucial steps since the measurement of the diffusion constant must be performed at extremely thin and light samples, irrespective of whether the transcrystalline layers were separated from the bulk or were prepared separately. The reliability of that technique with respect to reproducibility, and to systematic and statistical errors, was therefore carefully proven in advance.

## EXPERIMENTAL

### Materials and Preparation

The investigations were made at a commercial PP 1100N (Novolen) of the BASF Company. The first attempts to separate the transcrystalline surface of compact test specimens by means of a microtome in order to examine it separately failed. We changed over, therefore, to prepare the transcrystalline layers as they were separately, without the underlying bulk, as thin films. For this sake, an appropriate film was positioned between two substrate layers. This assembly was positioned in the hot stage of a polarization microscope (Mettler FP-5). The samples were melt-homogenized at  $220^\circ\text{C}$  for 5 min and then cooled down to ambient temperature with different cool-

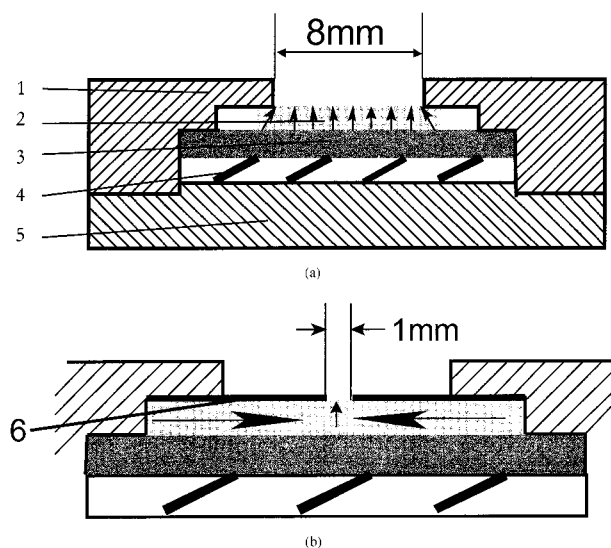
ing rates between 0.5 and 20°C/min. A slight pressure of 50 kPa was applied during crystallization in order to prevent creation of voids, which tended to develop upon crystallization at low cooling rates. The films for the observation of the structure development were between 100 and 200  $\mu\text{m}$  thick, whereas the materials for the diffusion measurements had thicknesses of 50  $\mu\text{m}$  or less.

For the sake of comparison, an amorphous sample was prepared by quenching a molten film in ice. The reliability tests were performed at a commercial low-density polyethylene film (LDPE) with a thickness of 73  $\mu\text{m}$ .

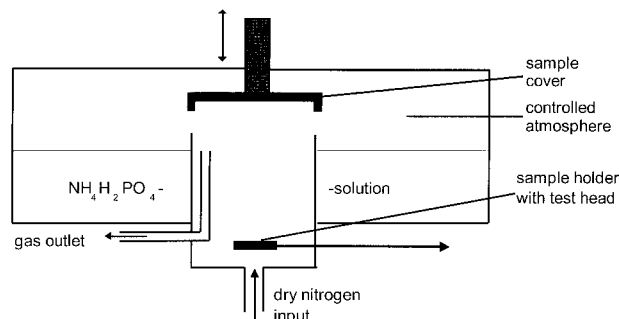
## Diffusion Measurement

### Technique

The diffusion coefficient was determined by suitable evaluation of sorption or desorption, respectively, measurements, that is, by the water uptake or loss  $\pm \Delta M(t)$  of the polymer film with time. The mass change can be detected by the corresponding change in the mechanical resonance frequency of the material. This may be performed by means of facilities that are initially intended for the determination of the thickness of sputtered layers on scanning electron microscopic



**Figure 1** Sketch of the test head and of sample geometry for absorption and desorption measurements. Arrows indicate the diffusion direction: ( $\uparrow$ ) transverse diffusion; ( $\rightarrow$ ) longitudinal diffusion. (a) Standard for transverse diffusion. (b) With diaphragm for the measurement of longitudinal diffusion: (1) Metal frame; (2) sample; (3) quartz supply; (4) spring mount; (5) ceramic sample holder; (6) diaphragm.



**Figure 2** Sample chamber. The cover and the valves for gas inlet and outlet, respectively, are closed during saturation. When starting the desorption measurement, the cylinder that contains the sample is closed by the cover, and dry nitrogen is applied. Then the weight loss with time is recorded.

samples (e.g., Leybold Heraeus Inficon XTC). Mass changes of less than  $10^{-8}$  g can be detected, which may be sufficient for the present measurements. In such devices, the sample under investigation lies on a quartz support, and the resonance frequency of this array is detected by the piezoelectric response of the quartz component. The measuring cell [Fig. 1(a)] is inserted into a chamber in which either dry air (nitrogen atmosphere) or water-saturated air (96% relative humidity over aqueous ammonium hydrogen phosphate solution) can be applied by opening or closing appropriate valves (Fig. 2). Either sorption or desorption measurement, respectively, is effectuated by a corresponding opening sequence of the valves.

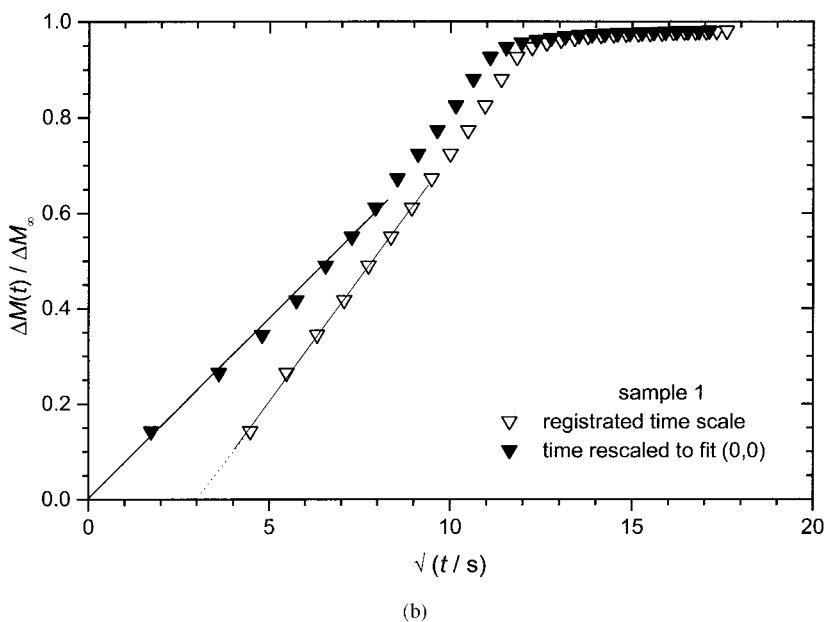
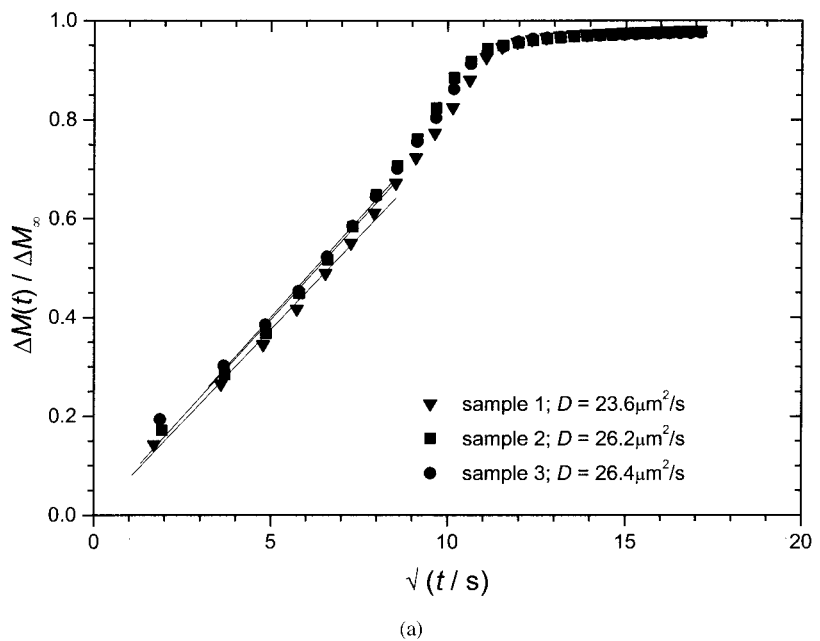
In the usual technique, water diffusion perpendicular to the film surface is detected [Fig. 1(a); transverse diffusion]. By insertion of an appropriate diaphragm, the diffusional direction can be turned round into a direction parallel to the surface, which then also allows the determination of the respective diffusion constant [Fig. 1(b); longitudinal diffusion].

### Mathematics

The diffusion coefficient  $D$  (usual unit:  $\text{cm}^2/\text{s}$ ;  $10^{-8} \text{ cm}^2/\text{s} = \mu\text{m}^2/\text{s}$ ) is defined by the second Fickian law,

$$\frac{\partial C(x, t)}{\partial t} = \frac{\partial}{\partial x} \cdot \left\{ \frac{\partial [D \cdot C(x, t)]}{\partial x} \right\} \quad (1)$$

where  $C(t, x)$  is the time ( $t$ ) and position ( $x$ ) dependent concentration of the diffusing sub-



**Figure 3** Reliability tests with commercial LDPE films of 73 μm thickness by desorption measurement upon transverse diffusion. Lines indicate linear fits in the appropriate representations: (a) Test of reproducibility; (b) test of time zero; (c) test of applicability of eq. (9); (d) test of necessary sorption time.

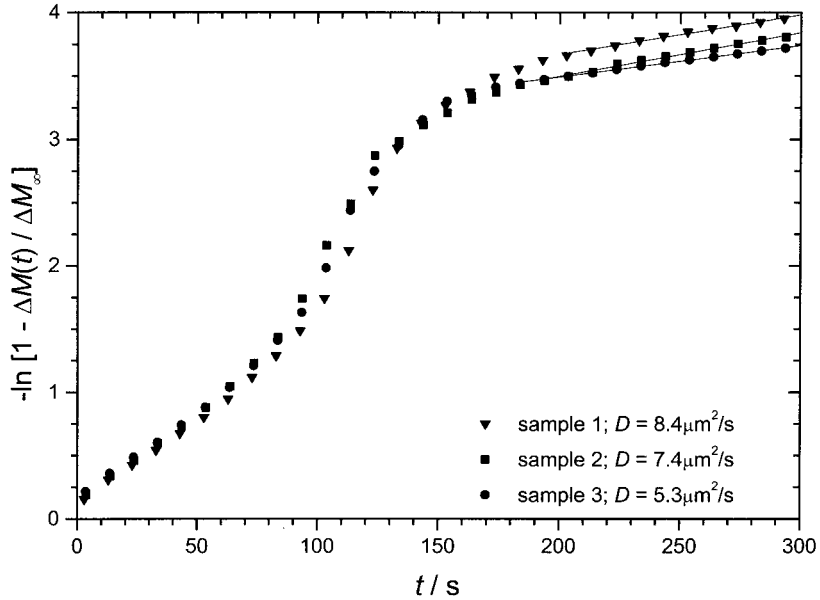
stance inside the carrier material.<sup>15,16</sup> In most instances,  $D$  can be assumed to be independent of composition.<sup>17</sup>  $D$  is linked with the permeation coefficient  $P$  and the solubility coefficient  $S$  by<sup>18,19</sup>

$$\frac{P}{D} = S \tag{2}$$

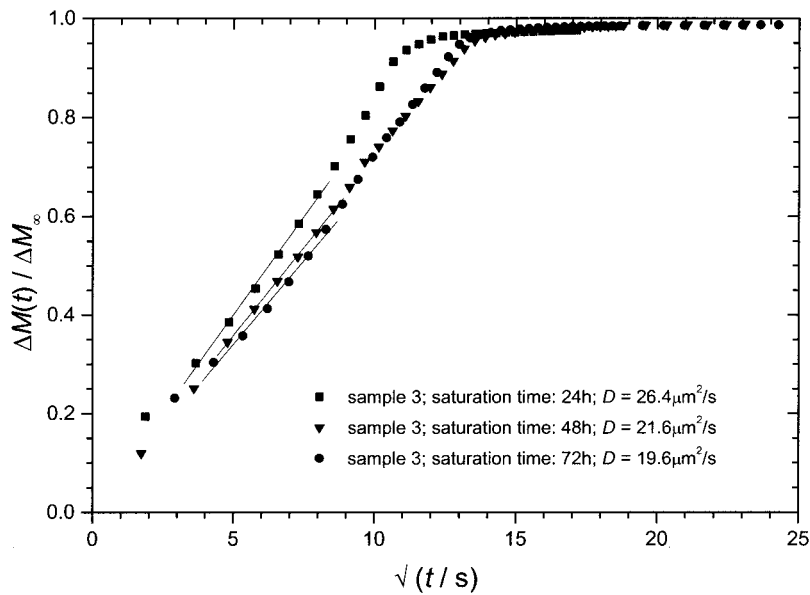
$P$  [unit: (cm<sup>2</sup>/s)/hPa] and  $S$  (unit: cm<sup>3</sup>/cm<sup>3</sup>), in their turn, are defined by

$$\Delta M(t) = \frac{P \cdot A \cdot t \cdot \Delta p}{d} \tag{3}$$

and



(c)



(d)

Figure 3 (Continued from the previous page)

$$\Delta C = S\Delta p \tag{4}$$

where  $\Delta M(t)$  is the mass of the diffusing material, which migrates into the film of thickness  $d$  and surface area  $A$  in the time  $t$ , if a pressure difference  $\Delta p$  between upper and lower surface is acting.<sup>20</sup> Only two of the parameters  $D$ ,  $S$ , and  $P$ , are consequently independent.

If, at the beginning of an experiment, the concentration at the one side of a sample is constant

and is zero inside (sorption condition), and if the other side is impermeable (since, e.g., the carrier material lies on a substrate), then

$$\frac{\Delta M_s(t)}{\Delta M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \times \exp \left[ -\frac{D(2n+1)^2 \pi^2 t}{4d^2} \right] \tag{5}$$

**Table I Reliability Tests with Commercial LDPE Films**

Sample	Transverse Diffusion Coefficient $D/\mu\text{m}^2 \text{ s}^{-1}$ by Evaluation of		
	Initial Slope [Eq. (7)]	Half-Width Time [Eq. (10)]	Final Slope [Eq. (9)]
1	23.7	23.6	8.4
2	26.1	26.2	7.4
3	26.7	26.0	5.3
Average	$25.5 \pm 1.6$	$25.3 \pm 1.4$	

Thickness of films: 73  $\mu\text{m}$ .

is a solution of eq. (1), where  $\Delta M_s(t)$  is the mass uptake by sorption, and  $\Delta M_\infty$  is the mass uptake in the sorption equilibrium.<sup>15,16</sup> For times  $t < \frac{d^2}{4D}$ ,

$$\Delta M_s(t) = \frac{2\Delta M_\infty}{d} \cdot \sqrt{\frac{D \cdot t}{\pi}} \quad (6)$$

is a sufficiently accurate approximation of eq. (5).  $D$  can then be determined from the slope  $F_1$  of the plot  $\Delta M_s/\Delta M_\infty = f(\sqrt{t})$  by

$$D = \frac{\pi}{4} F_1^2 d^2. \quad (7)$$

At long sorption times, respectively, that is, for  $t > \frac{d^2}{4D}$ , we have with sufficient accuracy

$$-\ln\left[1 - \frac{\Delta M_s(t)}{\Delta M_\infty}\right] = \frac{\pi^2 D t}{4d^2} + \ln\left(\frac{\pi^2}{8}\right), \quad (8)$$

and  $D$  is got as the slope  $F_2$  of  $-\ln[1 - \Delta M_s(t)/\Delta M_\infty] = f(t)$ :

$$D = \frac{4}{\pi^2} d^2 F_2. \quad (9)$$

Finally, the half-width time  $t_{1/2}$  of the process can be evaluated where  $\Delta M_s(t_{1/2})/\Delta M_\infty = 0.5$ , and  $D$  is found by

$$D = \frac{0.196d^2}{t_{1/2}}. \quad (10)$$

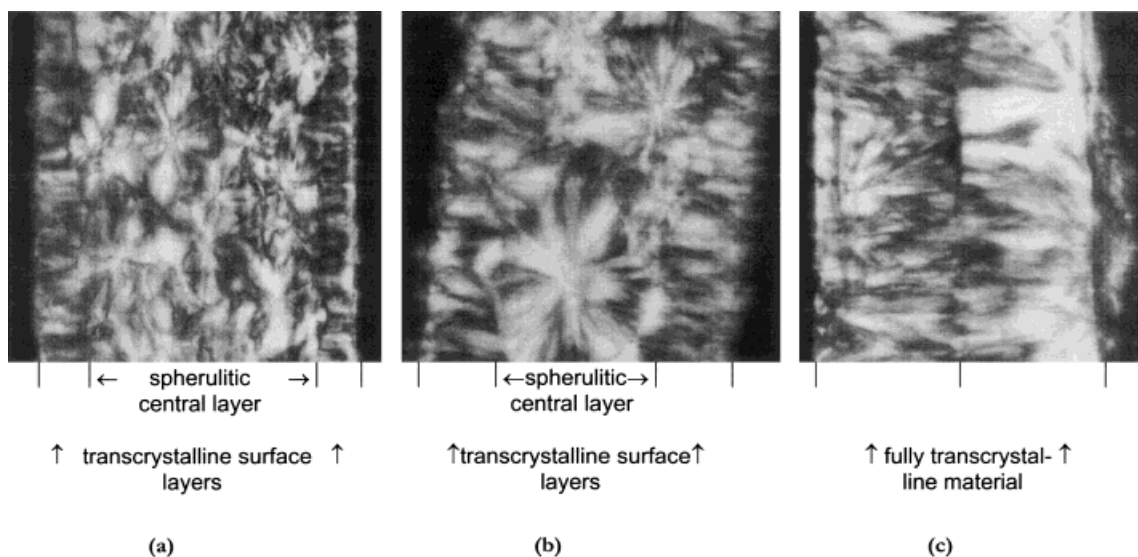
This equation follows from both eqs. (6) and (8). Adequate equations apply for desorption ( $d$ ) measurements, as follows:

$$\frac{\Delta M_s(t)}{\Delta M_\infty} = 1 - \frac{\Delta M_d(t)}{\Delta M_\infty}. \quad (11)$$

If eqs. (7) and (9) yield different values, this may hint at a composition dependence of  $D$  since one of these values relates to low and the other to high sorption, respectively.

**Reliability Tests with LDPE**

The used facility should, in principle, allow both absorption and desorption measurements. The former failed, however, for the present task since the mass uptake time is small compared to the time needed to achieve atmosphere equilibrium in the sample chamber after sudden change from dry to wet air due to the small sample thickness. Therefore, only desorption experiments were performed. For the sake of simplicity, no distinction is made between  $\Delta M_s$  and  $\Delta M_d$  in the figures. The reliability of the technique applied for transverse diffusion and that of the several evaluation routes [eqs. (7), (9), and (10)] had been tested by (1) investigating several samples (commercial LDPE films of 73  $\mu\text{m}$  thickness) of the same kind and (2) measuring a single LDPE sample several times. The result of (1) is displayed in Figure 3 and Table I. Figure 3(a) and Table I proof that the reproducibility is within 6% deviation when the evaluation is made according to eq. (7). The values found by evaluation of the half-width times fall into this range. In contrast, it must be concluded from Figure 3(c) that the evaluation of the end tail of the sorption curve according to eq. (9) fails. This equation uses essentially only the last



**Figure 4** Polarized light micrographs of the cross sections of transcrystalline i-PP samples crystallized on a PI substrate at cooling rates of (a) 20, (b) 10, and (c) 1 K/min. Film thickness: (a) 175 and (b and c) 125  $\mu\text{m}$ .

20% of the sorption, and these sorption values can be measured only with low precision. The discrepancy with those values derived from eq. (7) is too large to be due to a composition dependence of  $D$ . In any case, it is crucial that the sorption time zero, which may be distinct from the measuring time zero, must be found and suitably considered [Fig. 3(b)]. Similarly, experiment (2) exhibited the same values within an error range of 4% when evaluated by eq. (7), too.

The present value lies in the range of the experimental literature values which spread over the large range between 4,<sup>14</sup> 20,<sup>8</sup> and 66  $\mu\text{m}^2/\text{s}$ .<sup>21</sup> It should be recalled that the actual value depends crucially on the amount and the type of additives in the material under investigation and on its degree of oxidative degradation.<sup>21</sup>

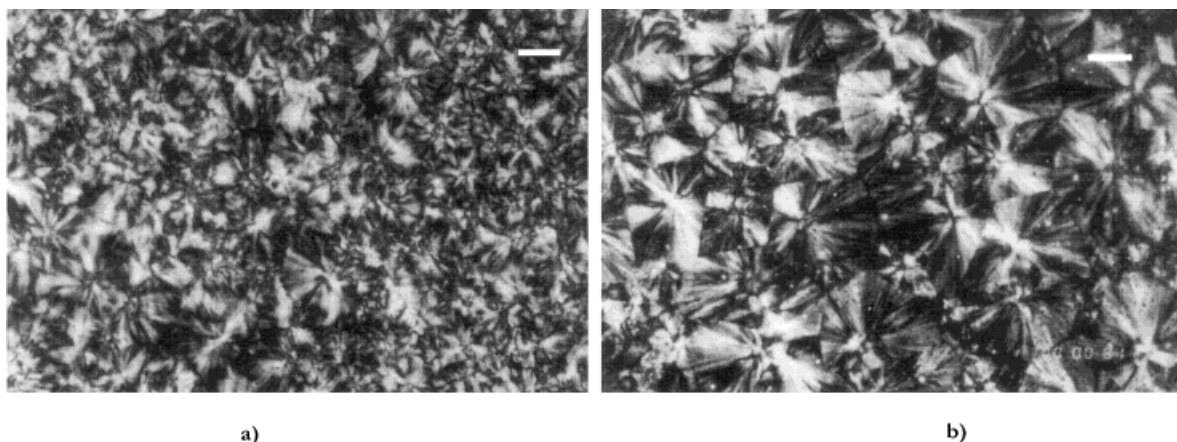
The chosen sorption time in advance for the reported specimen was 24 h. In the light of the foregoing remarks, it has therefore been tested which sorption time was necessary to get the necessary sorption equilibrium. Although it is clear from Figure 3(a) that most of desorption happens within few minutes, the samples may take up water for several days. It has indeed been found that sorption times of at least three days are necessary for the present investigations [Fig. 3(d)]. Only then, the calculated  $D$  values become independent on sorption time.

## RESULTS ON PP

### Transcrystallinity

Transcrystallinity developed between all polymeric substrates PI, PTFE, and PET. Metallic substrates like steel, copper, and aluminum yielded, in no case, transcrystallinity. Glass did not promote transcrystallinity either. The thicknesses of the transcrystalline layers increased severely with decreasing cooling rate (Fig. 4) if they develop at all. By suitable choice of the cooling rate, the structure could then be controlled between purely spherulitic and completely transcrystalline.

The extent of transcrystallinity, if it develops at all, is determined mainly by the ratio between the number densities of surface and volume nucleated spherulites, respectively: transcrystallinity is high if the former prevails. Since cooling starts at the sample surface, this holds, particularly at slow cooling rates. On the contrary, the specific features of the transcrystalline layers depend on the absolute number density of surface nuclei and, consequently, on the spatial number density of developing spherulites at spatial confinement. This number, in turn, also changes heavily with cooling rate (it decreases with decreasing cooling rate; Fig. 5) and is low with substrates of low transcrystalline efficiency. Clearly, the probability to develop volume spherulites decreases with de-



**Figure 5** Polarized light micrographs (top view) of transcrySTALLINE i-PP samples crystallized on a PET substrate at cooling rates of (a) 10 and (b) 1 K/min (film thickness, 100  $\mu\text{m}$ ; scale bar, 20  $\mu\text{m}$ ).

creasing sample thickness. Volume spherulites can, moreover, grow only two-dimensionally in thin samples and, as such, feign transcrySTALLINITY.

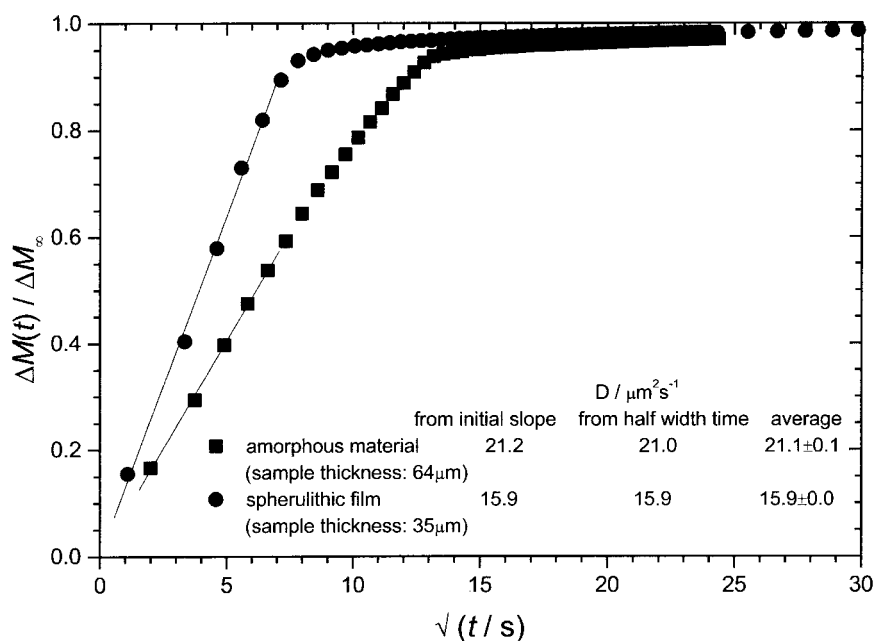
The samples for the diffusion measurements were prepared between PET substrates and had thicknesses of 50  $\mu\text{m}$  or less in order to prevent the development of volume spherulites. They exhibited, therefore, in any case, transcrySTALLINITY throughout the film where the cooling rate did not control the degree of crystallinity and the number of surface grown crystalline entities.

Details of the crystallization kinetics and of the crystalline structure are reported and discussed in a forthcoming article.<sup>22</sup>

## Diffusion

### *Amorphous and Spherulitic Materials*

The diffusion coefficient for amorphous i-PP films of 64  $\mu\text{m}$  thickness was found to be 21.1  $\mu\text{m}^2/\text{s}$  (Fig. 6). This value coincides well with the published one of 21  $\mu\text{m}^2/\text{s}$ .<sup>18</sup>  $D$  may depend, however,



**Figure 6** Water desorption curves of amorphous and of spherulitic i-PP (glass substrate; cooling rate, 10 K/min) by transverse diffusion.



**Table II Transverse Diffusion Coefficients of Transcrystalline i-PP (PET Substrate)**

Cooling Rate (K min <sup>-1</sup> )	Sample Thickness (μm)	D/μm <sup>2</sup> s <sup>-1</sup> by Evaluation of		$\bar{D}/\mu\text{m}^2 \text{ s}^{-1}$
		Initial Slope/[Eq.7]	Half-Width Time/[Eq. 10]	
10	32	12.2	12.1	12.2
5	47	10.9	10.7	10.8
1	48	9.6	10.0	9.8

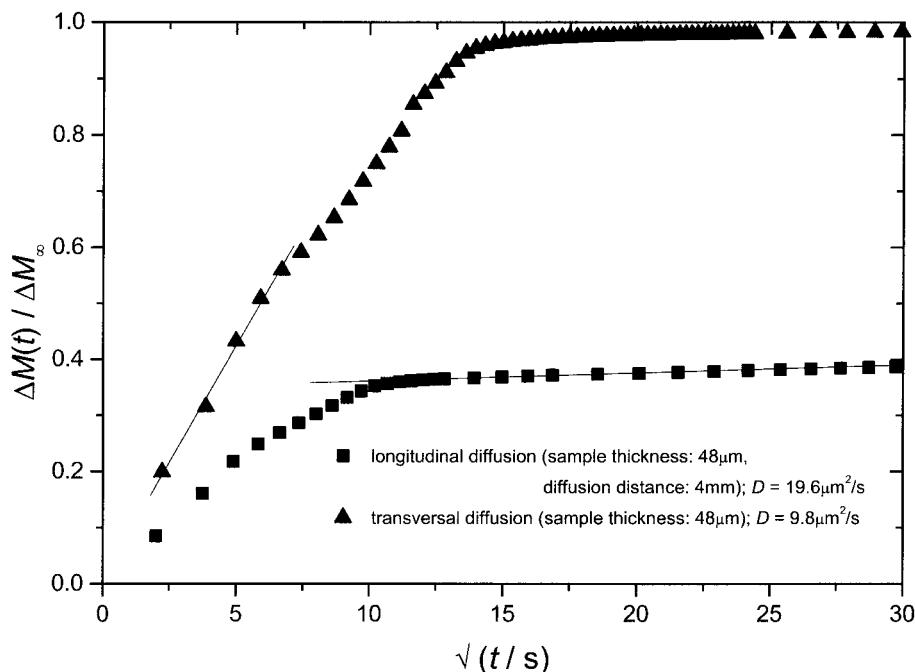
on thickness when the sample is smaller than 50 μm because of the existence of pinholes or voids in the sample.<sup>17,18</sup> Purely spherulithic material, as grown on a glass substrate at -10°C/min, on the contrary, exhibits a D of 15.9 μm<sup>2</sup>/s. At that thermal condition, the largest spherulites have a diameter around 20 μm (cf. Fig. 5) and are consequently smaller than the sample thickness. The majority of the spherulites are therefore grown three-dimensionally.

#### Transcrystalline Material

The transverse diffusion coefficients in materials of different transcrystalline structure as induced by different cooling rates are to find in Table II. The values are around 10 μm<sup>2</sup>/s and decrease

slightly with decreasing cooling rates. This must be related to the observation that faster cooling causes finer transcrystalline texture, that is, smaller lamellar bundles, and a larger number of surface grown supermolecular entities.

Insertion of a diaphragm into the test head (Fig. 1) allows measurement of desorption curves upon longitudinal diffusion. Performing this experiment and its evaluation are crucial, however, for several reasons. First, due to the small exit ( $\approx 1 \text{ mm}^2$ ), sorption and desorption times are rather long. Second, eqs. (7), (9), and (10) are only roughly applicable since the geometry will now be cylindrically symmetric instead of linear. The exact equations for the present geometric conditions are rather complicated, however, and hard to



**Figure 7** Longitudinal and transversal diffusion through transcrystalline surface layers (PET substrate; cooling rate, 1 K/min).

handle. Measurements of longitudinal diffusion and its evaluation by these means will therefore be less accurate than those of transverse one. We believe, however, that use of eqs. (7), (9), or (10) will nevertheless yield sufficiently reliable information on the longitudinal diffusion behavior. In Figure 7, a corresponding desorption curve for a transcrystalline surface layer grown on PET substrate upon cooling by 1°C/min is displayed. The initial slope in that curve is ruled by fast desorption due to some transversal diffusion from the central part of the sample. The gradual increase for longer times, which also follows a  $\sqrt{t}$ -law, is then caused, indeed, by the longitudinal diffusion. From that part of the curve, a longitudinal diffusion coefficient of  $19.6 \mu\text{m}^2/\text{s}$  can be deduced. This has to be compared with the value of  $9.8 \mu\text{m}^2/\text{s}$  for the transverse diffusion through the same material.

## CONCLUSION

We start remarking that diffusion, in any case, is possible only through the amorphous phase of that semicrystalline material and must be highest, consequently, in purely amorphous samples. This is indeed confirmed. In partially crystalline PP, in contrast, desorption is performed by migration of the diffusing molecules along paths through the inter-connected amorphous parts in the material, for which we introduce the term "amorphous percolation network". The widths of the paths in that network depend on the actual degree of crystallinity and on the actual supermolecular morphology. The network is composed of three groups of paths. There are the small paths between the crystalline lamellae, the broader roads between the lamellar bundles, all within a spherulite, and, finally, the comparably broad streets between the spherulites and at the spherulites surfaces. The connectivity of the network and its percolation ability is determined by the relative contributions of these three groups and the average width of their elements. It depends also heavily on the amorphous texture of the material, that is, on the average orientation of the several paths and the chain orientation therein. Finally, the outlet ability of an individual path is influenced by its mass density, that is, the amorphous density at the particular location. Beside the diffusion through the material, the contributions of

voids, holes, or similar structural distortions must clearly be considered, too.

The present results can be understood well on basis of these considerations. It should be recalled that the occurrence of holes or voids was prevented by careful preparation. The rapidly cooled i-PP was a finely spherulitic material with low crystallinity and with rather small three-dimensionally grown, isotropic spherulites. Its diffusion coefficient ( $16 \mu\text{m}^2/\text{s}$ ) is consequently slightly smaller than that of amorphous material ( $21 \mu\text{m}^2/\text{s}$ ). In contrast, the transverse diffusion ability through transcrystalline material is very low (around  $10 \mu\text{m}^2/\text{s}$ ). This indicates that the amorphous paths are oriented mainly parallel to the surface. Accordingly, the coefficient of longitudinal diffusion is rather high ( $19 \mu\text{m}^2/\text{s}$ ) and close to that of purely amorphous material. The average of the longitudinal and transversal diffusion coefficients is roughly that of spherulitic isotropic material. The transversal diffusion coefficient of transcrystalline i-PP decreases with increasing transcrystalline order, again in accordance with the conclusion that the amorphous paths are oriented parallel to the surface. This transcrystalline order is obviously enhanced by coarser supermolecular structure, by reduction of the number of surface grown supermolecular entities, and by increasing crystallinity within the latter.

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