NMR Microscopy of an "Anisotropic" Polymer

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Summary: Two different samples of high-density polyethylene (HDPE) have been studied. One (isotropic) is extracted from the material core whereas the other (anisotropic) involves two sides which have been in contact with the injection mold. It is observed by NMR microscopy (using radiofrequency field gradients) that these two sides favor toluene penetration into the material. The distribution of toluene nuclear spin relaxation times (extracted from proton T_1 and T_2 images) exhibits likewise important differences between the two samples. These differences can be accounted for by partial molecular ordering at the vicinity of the "mold sides". Finally, in investigating the anisotropic sample (without solvent), three different phases (two amorphous and one crystalline) are revealed by ^{13}C chemical shift imaging experiments (performed with radiofrequency field gradients under CP/MAS conditions). Each amorphous component is preferentially present at one of the two "mold sides".

Keywords: NMR; polyethylene (PE); solid-sate ^{13}C chemical shift imaging; solvent diffusion imaging

Introduction

Polyethylene is a semi-crystalline polymer widely used as a construction material because it represents an excellent compromise between mechanical properties, weight and cost. A complication with semi-crystalline polymers comes from their ability to develop an inhomogeneous morphology from surface to bulk, depending upon the processing technology (extrusion, injection molding...). Such heterogeneity, called a "skin effect", often originates from the strong temperature gradient, which is occurring during cooling between surface and core. We intend here to study more specifically the impact of this "skin-effect" on the diffusion of toluene in high-density polyethylene, and eventually to investigate the material alone. NMR imaging techniques based on radiofrequency field gradient methodology will be used. They include spin density and

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relaxation time images for studying the solvent within the polymer and solid-state ^{13}C chemical shift imaging for detecting the different phases of the polymer.

The material is a high-density polyethylene (HDPE) with density equal to 0.96. The melt flow index is 7g/10mn at 190°C and under a weight of 2.16kg. This is an industrial product provided by AtoFina. 2 and 4mm thick plates have been injection molded. Two types of samples were prepared for NMR studies :

- from the 4mm thick plates, a 1mm thick skin was eliminated on each side of the plates, thus reducing their thickness to 2mm. Such plates consist of core material only and therefore these samples will be referred to as "isotropic" in the rest of this paper.
- from the 2mm thick plates, bars were machined without further preparation. These samples will be denoted "anisotropic" because their four sides are not identical. Two opposite sides correspond to the original surfaces of the plates in contact with the injection mold. The other two opposite sides were cut in the bulk of the plates and correspond to core material.

Preliminary to NMR measurements, the morphology of these samples was investigated at two different scales using optical microscopy and TEM. Contrary to the isotropic sample (or to the sides of the anisotropic sample cut from the bulk) which is homogeneous up to the surface with a spherolitic morphology (figure 1A), the sides of the anisotropic sample having been in contact with the injection mold are characterized by a skin of ca. 30μm located at the surface of the sample (figure 1B). This skin appears homogeneous at the scale of optical microscopy (no morphology is visible) indicating that the crystalline objects, if any, are smaller than ca. 0.3μm. Beyond the skin, the sample exhibits a fine spherolitic morphology. The TEM picture of the skin (figure 1C) shows that it consists of thin lamellae aligned along a single direction perpendicular to the surface of the sample.

Among the various microscopy techniques, NMR imaging is probably the only one that makes it possible in situ investigation of the bulk material (or solvent within the material) in a non-invasive and a non-destructive way. However, the technique does not afford such a good spatial resolution as the other methods which are conversely limited to the examination of the surface at a very limited depth. Beside the poor spatial resolution, classical NMR microimaging (using gradients of the static magnetic field, also called B_0 gradients) may suffer from severe artifacts arising from differences of magnetic susceptibility within a heterogeneous sample.

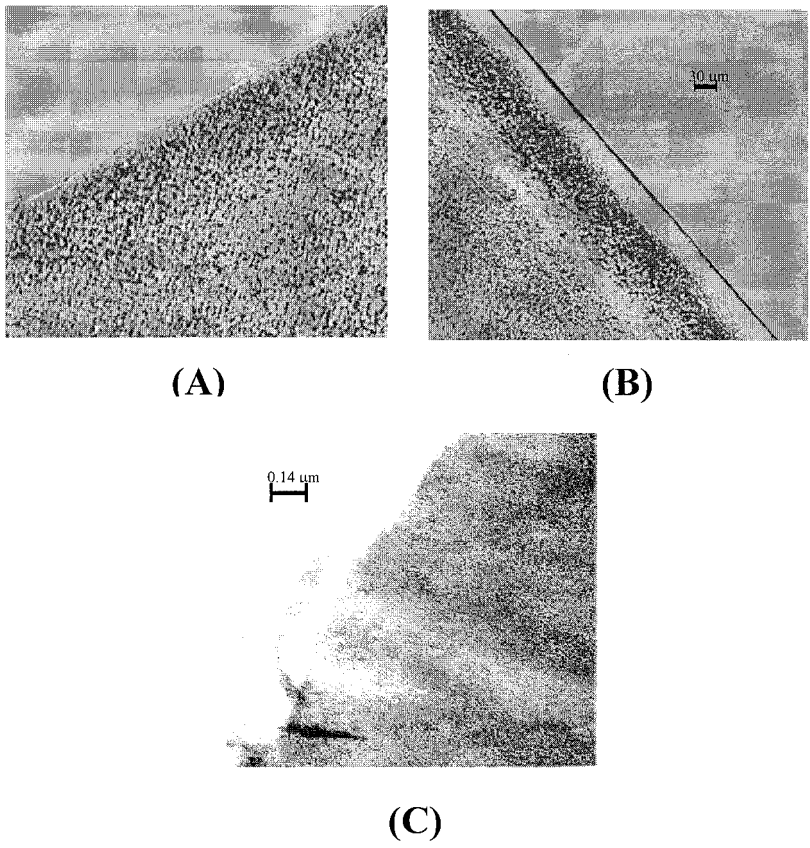

Figure 1. Images obtained by optical microscopy: (A) isotropic HDPE, (B) anisotropic HDPE exhibiting a "skin effect" at the surface which was in contact with the mold. (C) TEM image showing in detail the "skin" of (B).

The experimental imaging method used here is based on gradients of the other magnetic field

employed in a NMR experiment namely the radiofrequency field[1] (also denoted B_1 gradient). Its advantages are i) to be totally insensitive to variations of magnetic susceptibility, ii) to be less sensitive to short transverse relaxation times than imaging with B_0 gradients. They should therefore be well adapted to the present study.

Diffusion of toluene in HDPE

Typical NMR images taken for various absorption times with pure toluene are shown in Fig.2A and 2B for "isotropic" and "anisotropic" samples, respectively (HDPE samples were immersed in toluene for the specified absorption time and removed from the solution for NMR measurements). The intervals between measurements were chosen in order to analyze correctly the whole process of absorption, from the beginning to saturation, and therefore are not the same for the two samples. It is apparent from figure 2A that the absorption process proceeds at similar rates through all sides of the isotropic sample. The isovalues of toluene concentration exhibit circular contours in the inner regions of the sample, while the outer shape of the sample is close to a square. Such a behavior is characteristic of a Fickean diffusion process. By contrast, we can see from Fig.2B that the first stage of absorption in the "anisotropic" sample is itself anisotropic, this anisotropy being related to the sides of the sample. Indeed, the image shows clearly that the solvent migrates primarily through the surfaces that have been in contact with the injection mold. These sides will be denoted "mold sides". The other two sides, which were cut in the bulk of the plates, involve a much slower migration of the solvent. Eventually the solvent fills up the sample uniformly, as confirmed by the image obtained after 100 hours of immersion although this state is probably reached before. Some contours close to the surfaces still remain. They reflect a gradient of solvent concentration at the surface which is likely caused by some desorption occurring during the measurement itself.

These images can be sucessfully simulated[2] by using the second Fick's law[3]

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial c}{\partial y}\right) \qquad (1)$$

c is the concentration (or any variable proportional to the concentration, for instance the spin density) and D is the diffusion coefficient which is assumed to be of the form[4]

$$D = D_0 + D_1\left(\frac{c}{c_\infty}\right)^2 \qquad (2)$$

where D_0 and D_1 are constants, c and c_∞ are the toluene concentration (or spin density) in the sample and at saturation respectively. As the simulations reproduce the essential trends of the experimental images and since they are just derived from surface boundary conditions (in addition to the expression of the diffusion coefficient (eq. (2)), we have a further indication of the peculiar nature of the anisotropic sample "mold sides" and of its partial ordering which favors solvent penetration.

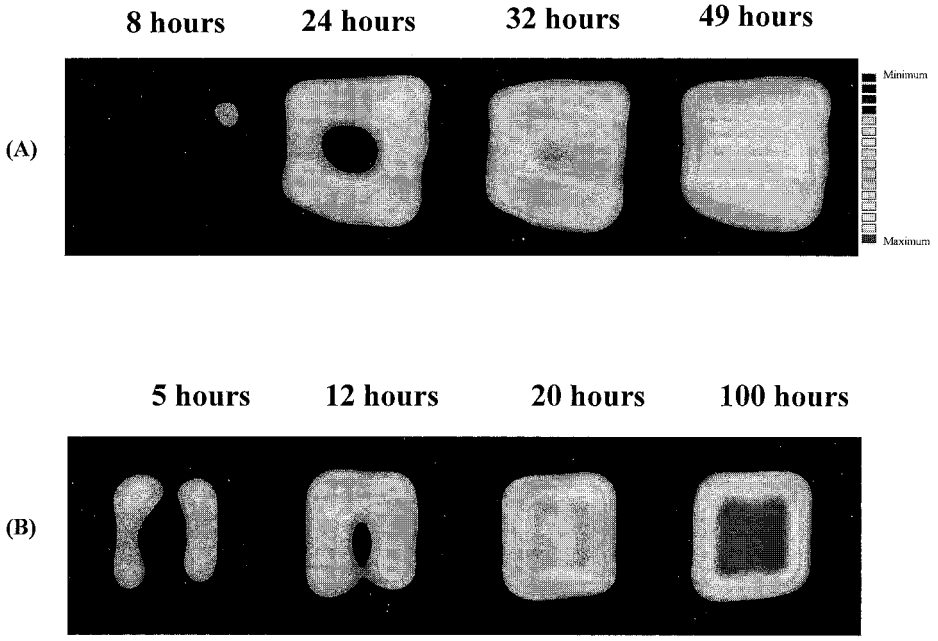

Figure 2. NMR spin density images obtained by B_1 gradient techniques. HDPE was immersed in toluene for the time indicated above each image. (A) isotropic sample; solvent penetration is the same for the four sides. (B) anisotropic sample; the "mold sides" (see text) favor solvent penetration.

Nuclear relaxation time images of toluene embedded in HDPE

The method we are currently using in the context of B_1 gradient imaging consists primarily of replacing the standard signal acquisition in a classical relaxation time measurement by the imaging procedure. In fact, either the longitudinal relaxation time T_1[5] or the transverse relaxation time T_2[6] can be obtained accurately by choosing adequately two points of the evolution curve provided that they are acquired in alternate blocks, this mode affording compensation for any instrumental drift. For instance, if T_2 is to be measured by the widely used CPMG method (which employs a train of π radio-frequency pulses separated by a time interval of 2τ), these two points correspond to c_1 and c_2 cycles in the pulse train. A pixel-by-pixel analysis leads to the required T_2 map assuming only one T_2 for each pixel :

$$T_2 = \frac{-2\tau(c_2 - c_1)}{\ln(\frac{S_2}{S_1})} \tag{3}$$

where S_1 and S_2 are the signal intensities in blocks 1 and 2, respectively. The duration of relaxation time imaging experiment is therefore only twice the one of a normal spin density imaging experiment.

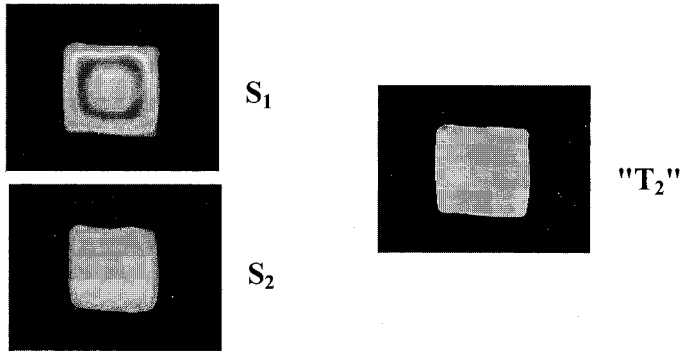

Figure 3. Left: spin density images partially relaxed through the transverse relaxation time (S_1 and S_2 correspond to c_1 and c_2 cycles of the CPMG pulse train with $c_2 > c_1$).
Right: T_2 image obtained by application of eq. (3) to each pixel.

A typical example is shown in figure 3. In spite of "partially relaxed" spin density images exhibiting clearly a heterogeneity of toluene concentration (shortage of toluene can be seen at the center of the sample; Fig. 3), the T_2 map is much more uniform, indicating that toluene transverse relaxation time is quasi constant, regardless of the actual concentration at a given location within the sample. Although small, the differences in T_2 or T_1 values observed in each map are significant with regard to the experimental uncertainty, but cannot, at first sight, be associated with any morphological property. It must however be borne in mind that a given pixel encompasses a very large area at the macromolecular scale and thus can be representative of several different structural features (e.g. amorphous, crystalline, oriented...) with unpredictable proportions (and possibly varying randomly from one experiment to the other). We have thus represented the distribution of toluene relaxation times in the form of histograms (figure 4) and subsequently fitted this distribution according to gaussian functions with the hope to gain some insight into the structural properties of the polymer sample. We can notice a strong asymmetry (involving two well-characterized gaussian functions) for "anisotropic" HDPE after an immersion time of 30 hours whereas essentially a single gaussian function described the distribution in the "isotropic" sample after the same immersion time; this is also true for "anisotropic" HDPE at saturation. For these two latter samples, the distribution exhibits nearly the same shape.

We can explain the asymmetric distribution in "anisotropic" HDPE after 30 hours of immersion (figure 4B, left) by the particular structure of the two "mold sides" and assign the minor component to toluene closed to these sides. Indeed, when toluene penetrates the polymer by the skin (and solvent uptake occurs preferentially that way), its local environment is more organized and the fact that T_2 is larger can be understood from the unique property of transverse relaxation rates which are dominated by spectral densities at zero frequency if slow motions are present (this is certainly the case here due to the interaction of the solvent with the polymeric matrix). Relying for instance on a simple model such as the one of Lipari and Szabo[7] yields

$$\frac{1}{T_2} \approx K\tau_c S^2 \tag{4}$$

where K is a scaling factor related to the interactions affecting the toluene protons, τ_c a correlation

time associated with slow motions and S an order parameter which characterizes the degree of organization of regions close to the "mold sides". As $-0.5 \leq S \leq 1$, T_2 is smaller in these regions than in regions with little organization (figure 4B, left).

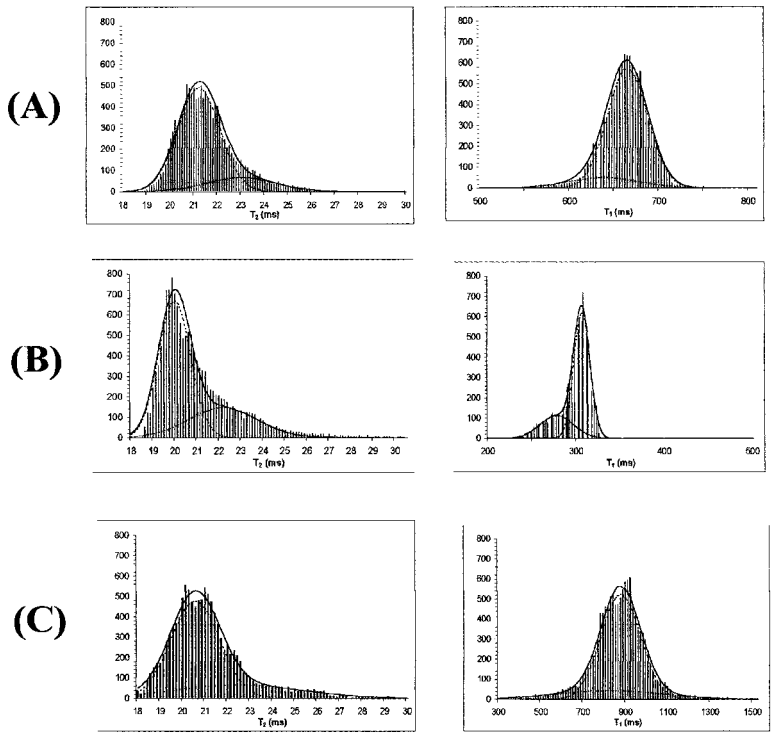

Figure 4. Histograms showing the toluene T_2 (left) and T_1 (right) distributions (derived from images such as the one of fig. 3) within (A) an isotropic sample immersed for 30 hours in toluene, (B) an anisotropic sample for the same time of immersion, (C) an anisotropic sample at saturation of toluene.

As far as longitudinal relaxation times are concerned, fast motions become predominant whenever they coexist with slower motions (those being described by correlation times of the order of the nanosecond or larger). This is due to the fact that longitudinal relaxation rates involve spectral densities at the measurement frequency and at twice this frequency, in such a way that the

contribution from slow motions essentially vanishes. Consequently, one is left with fast rotational motions which depend mainly on the size and on the nature of free-volume in which the solvent molecules are moving. This free-volume being related to swelling processes, we can conceive it is smaller or of different geometry in the more organized part of the material (regions close to the "mold sides" in the anisotropic sample) thus inducing some hindrance of the fast motions and yielding smaller T_1 (see the minor contribution in figure 4B, right). Also, for this sample, as the swelling proceeds more slowly, the created free-volume would be smaller; this would explain that T_1 are globally smaller than for the "isotropic" sample (compare figures 4A and 4B, right).

Of course, after a long time of immersion, any organization tends to disappear due to the swelling processes and symmetric distributions similar to that of the "isotropic" sample are retrieved (compare figures 4C and 4A). Finally, due to their strong relation with swelling processes, it appears normal that the T_1 distributions are not centered on the same value.

^{13}C chemical shift imaging of anisotropic HDPE

The objective is now to study directly the material morphology, thus to rely on solid state NMR methods. Obviously, the ^{13}C CP/MAS/DD experiment is the more appropriate. What is needed is a space encoding procedure. Because of sample spinning, we have no other choice but to investigate the sample along the only spatial direction which is fixed, namely the spinning axis. Again, we resorted to radiofrequency field gradients and built a special probe[8] with a double turn coil, the axis of which coincides with the spinning axis and which therefore delivers a radiofrequency field gradient in that direction. It can be noted that the standard coil must be modified in order to be orthogonal to the gradient coil. Chemical shift imaging is performed by means of the conventional CP/MAS/DD sequence in which a gradient pulse, of duration t_1, is inserted before signal acquisition with which is associated the time domain t_2. A double Fourier transform with respect to t_2 and t_1 yields chemical shift information along the ν_2 frequency domain and one-dimensional spatial information along the ν_1 frequency domain.

Of course, the spatial resolution is not sufficient for observing directly the skin at the mold sides. However, the ^{13}C spectrum of HDPE exhibits (in addition to a main peak assigned to the crystalline component) a broad shoulder assigned to amorphous phase(s). If the sample is cut from the plate so that the mold sides are perpendicular to the spinning axis, we can hope to detect a

possible non-uniform spatial distribution of the different phases. However, because of the strong spectral overlap, this can be attempted only if we are able to separate the signals corresponding to crystalline and amorphous components. The most efficient way is to rely on ^{13}C longitudinal relaxation times T_1, as the one of the crystalline phase is much longer than the one of the amorphous phase(s).

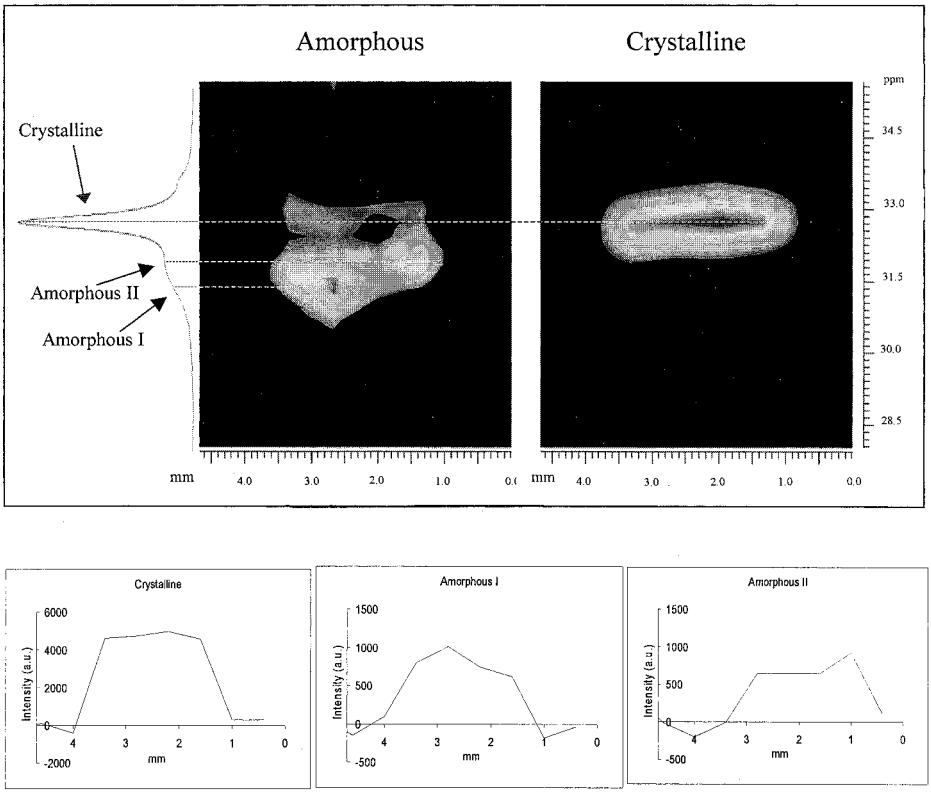

Figure 5. Top: Chemical shift imaging results of anisotropic HDPE with two different maps for the crystalline phase (right) and amorphous phases (left). The vertical dimension corresponds to chemical shift (with a reference spectrum along the relevant axis), whereas the horizontal dimension corresponds to spin density along the spinning axis.
Bottom: Distribution of the three phases along the spinning axis (it can be remembered that the "mold sides" are the two extremities), obtained by projections of the two-dimensional maps along a vertical direction.

The trick is, after the cross-polarization stage, i) to take the magnetization toward the z axis for one experiment and to -z for another experiment, ii) then to let relaxation take place for a time such as magnetization of amorphous phase(s) reaches thermal equilibrium whereas magnetization of crystalline phase remains essentially unchanged. Subtraction of the two experiments then yields the chemical shift image of the crystalline phase while the addition provides the amorphous component image(s). This method has been applied to anisotropic HDPE[9] and results are displayed in figure 5. We can observe that if the crystalline phase is evenly distributed, there are clearly two amorphous phases differentiated by their chemical shift, each of them being preferentially located close to one of the "mold sides". These observations confirm their particular morphology and demonstrate that each side is different. This is a visualization of the effects of the cooling process (which, moreover, does not occur in the same conditions for the two mold sides), in contrast with the isotropic sample (results not shown) which, as expected, shows up only one amorphous phase, evenly distributed.

Conclusion

The so-called "anisotropic" HDPE presents a particular morphology in regions close to sides having been in contact with the injection mold. These regions are partially ordered as shown consistently by different experimental results:

- This partial order allows for an easier solvent penetration (than in "isotropic" HDPE) as evidenced by simple spin density images.
- Solvent T_2 and T_1 distributions correspond to single gaussians for isotropic HDPE, whereas two gaussians are observed in the case of anisotropic samples. The minor one arises from the ordered regions and the relaxation time values can be interpreted accordingly.
- Chemical shift imaging of the material itself indicates that these regions are rich in amorphous phases, while the crystalline phase is evenly distributed. Moreover, two different amorphous phases, corresponding to the two mold sides, can be detected. This indicates distinct cooling conditions during polymer fabrication.

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