Communications to the Editor

Line-Broadening Effects for ^{129}Xe Absorbed in the Amorphous State of Solid Polymers

Inspired by the success of ^{129}Xe NMR in the study of the void space in microporous solids, there is now an increased interest in the possibilities of ^{129}Xe NMR for the characterization of the amorphous phase of solid polymers. In the early applications of ^{129}Xe NMR to zeolites and clathrates, it was recognized that a correlation exists between the isotropic ^{129}Xe shift and the free space that the Xe atoms have at their disposal at the trapping site.[1,2] Theories have emerged that correlate the isotropic shifts with the mean free path of the xenon in the void space of a zeolite,[3] the surface curvature of zeolite pores and cages,[4] and the diameter of the cages in clathrate hydrates.[5] As Ripmeester and Ratcliffe[6] pointed out recently, the strength of the sorption sites plays an important role in the interpretation of Xe chemical shift data. In the case of so-called weak sorption sites, where only van der Waals interactions are important, they showed, using model calculations on spherical cages, that the strength of the binding site is intimately linked to its ability for efficient contact with xenon atoms; i.e., a spherical cage that exactly matched the van der Waals radius of the xenon atom forms the strongest binding site. For large cages sorbed xenon will partition its time between a sorbed and a free state, and thus the observed chemical shift will be a function of the sorption energy, the void space, and the temperature. All these factors make the interpretation of ^{129}Xe NMR data in ill-defined materials such as amorphous and semicrystalline polymers very difficult. So far only a few ^{129}Xe NMR studies of polymers have appeared in the open literature. Stengle and Williamson[7] found that the variation of the line width of xenon in poly(ethyl methacrylate) as a function of temperature changed at the glass transition temperature. They assumed that the observed line narrowing with increasing temperature was associated with an increasing exchange rate of xenon among various environments within the amorphous phase. Furthermore, they observed two lines in a LLDPE sample, which has been associated with two different subregions in the amorphous phase. Kennedy[8] observed several lines in EPDM rubber and noted a change of the spectral features upon curing of the sample. Brownstein et al.[9] studied a series of polystyrene–polyisoprene block copolymers. They were able to observe separate lines for the two microphases in the copolymer. For a small diblock copolymer, however, only one line was observed, this was attributed to a fast exchange of xenon between both phases.

As becomes obvious from the discussion above, ^{129}Xe NMR holds some promise for the study of amorphous polymers as different environments are observed. It can be expected that a distribution of trapping sites exists in the amorphous region of a polymer, leading to fairly broad lines. Moreover, different subregions may exist within a sample. An important factor is, however, if and on what time scale exchange takes place between different regions. Furthermore, other sources of line broadening, not related to a distribution of environments may be present. In this paper we present our first ^{129}Xe NMR results of several polyethylene samples and a polycarbonate sample addressing these questions.

Linear low-density polyethylene (LLDPE, density 922 kg/m^3, melt index I-2 = 2 dg/min), low-density polyethylene (LDPE, density 921 kg/m^3, I-2 = 2 dg/min), and high-density polyethylene (HDPE, density 960 kg/m^3, I-2 = 0.35 dg/min) were obtained from the DSM Research Laboratories. Polycarbonate (PC) was obtained from the Philips Research Laboratories. The NMR samples were prepared in 7- and 10-mm tubes as described by Stengle and Williamson.[7] NMR spectra were obtained on a Bruker WM 200, a Bruker CXP 300, and a Bruker AM 500 spectrometer, operating at a frequency of 55.4, 83.0, and 138.4 MHz for ^{129}Xe, respectively. Spectra were recorded in a conventional broad-band high-resolution probe. On the 500-MHz spectrometer, a 7-mm solid-state probe was also used. Chemical shifts are quoted with respect to the free-gas peak, without pressure correction.

At room temperature the spectra of all three polyethylene samples look similar, with a chemical shift of approximately 200 ppm, and a line width of $\approx$100 Hz at 4.7 T, only the HDPE sample has a slightly broader line. The main difference of the spectra is the signal to noise ratio, which is much lower for the HDPE sample. This is in accordance with the assumption that the xenon is indeed only dissolved in the amorphous part of the polymer, as the crystallinity of HDPE is much higher as compared to the LDPE and LLDPE sample. For different samples small variations of the chemical shift are observed, which may be due to variations of the pressure in the tubes. This makes it difficult to compare the shifts of the three samples. However, by physically mixing the LDPE and HDPE samples we observed two lines, with a shift difference of 3 ppm, which means that the local xenon environment is slightly different in these samples.

Measurements as a function of the magnetic field strength show that the line width increases linearly with the field for all three polyethylene samples. So the line shapes are due to a distribution of chemical shifts or a small residual shielding anisotropy. This linear field strength dependence of the line width suggests that there is no exchange of xenon between the different regions on the time scale of the inverse line width. In order to establish if there is any slow exchange, we performed a 2D exchange experiment on the LLDPE sample with a mixing time of 2 s. As can be seen in Figure 1, the spectrum consists of a resonance that is extended along the diagonal. This means that there is no diffusion of xenon between different regions in the sample, allowing a ^{129}Xe spin to sample different local environments, on the time scale of seconds. On the other hand, when we compare the spectra to those of (crystalline) clathrates and zeolites, the line width seems to be remarkably narrow to reflect a distribution of void spaces in the amorphous part of the polymer. We must keep in mind, however, that the polyethylene samples are above their glass transition temperature at room temperature; i.e., the molecular chains have a great mobility. So the xenon atoms will experience an "averaged" environment due to the great chain mobility. The inhomogeneous line broadening may then be explained to

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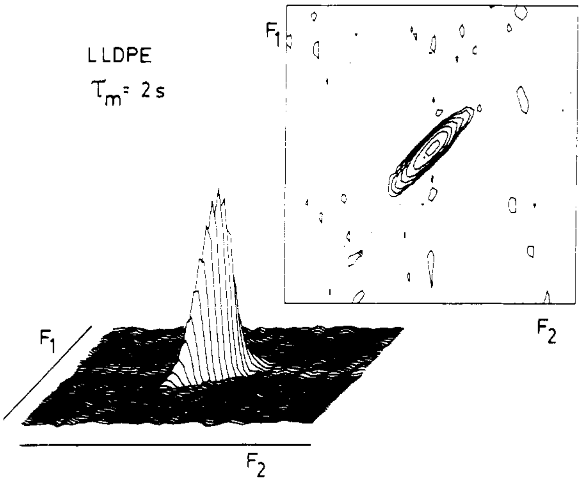

Figure 1. 2D exchange spectrum of ^{129}Xe in LLDPE recorded by TPPI. Apparently there is no exchange of xenon between regions with a different local field within the mixing time of 2 s.

be due to different susceptibilities in different parts of the samples originating from the distribution of crystalline lamellae in the sample. This would also explain the slightly bigger line width in the more crystalline HDPE. From the 2D experiment we can now conclude that, within 2 s, there is no exchange of xenon between regions in the sample with different susceptibilities. Possibly, the crystalline lamellae hinder the diffusion of xenon through the amorphous part of the polymer. A local exchange of xenon between regions with a rather constant magnetic field can, of course, not be excluded.

Spin–lattice relaxation measurements of ^{129}Xe in HDPE, LDPE, and LLDPE showed no significant difference in T_1 ($\approx$10 s) for all three samples. More importantly, the T_1 relaxation time appeared to be independent of the magnetic field strength. This implies that relaxation takes place via the spin rotation mechanism, indicating that there is no strong interaction of the xenon with the polymer.

A very different situation arises in the completely amorphous polycarbonate (PC), which is below its glass temperature at room temperature. At 4.7 T a 500-Hz wide line at 212 ppm is found. Although the line is broader than those for the PE samples, it still seems fairly narrow to reflect a broad distribution of sites available to xenon. Experiments at 11.7 T show a line width of 2000 Hz, i.e., a more than linear increase of the line width with the field strength. This suggests that there is indeed a distribution of different void spaces in the polycarbonate, but xenon can exchange between these sites on the NMR time scale. If we consider the spread in the resonance frequency, without exchange, due to a distribution of shifts, expressed in hertz, this will be smaller at a field strength of 4.7 T compared to a 11.7-T field. In case exchange processes take place between various sites, at such a rate that the fast-exchange limit has not yet been reached, it may well be that the extent of exchange narrowing is larger at a field of 4.7 T compared to 11.7 T. In other words, the observed line at 11.7 T is more than 2.5 times broader than the line at 4.7 T. That exchange indeed takes place has been confirmed by a 2D exchange experiment (Figure 2). We now observe a round line shape, indicating that a xenon atom can probe every resonance position in the total shift distribution within 1 s.

In order to gain more insight in the xenon–polymer interactions in relation to the chain mobility, we measured ^{129}Xe NMR spectra of xenon in the polyethylene samples as a function of temperature from room temperature down to −40 °C, which is just below the β-transition temperature. For all samples we register a gradual increase of the line width down to −20 °C. At −40 °C, however, a strong increase of the line width is observed, which is most pronounced for the LDPE sample (Figure 3). The β-relaxation in polyethylene is related to branching of the polymer. In linear PE the β-transition is very weak. It is thought that the β-relaxation originates from the interfacial regions, which increases strongly in more branched samples.[10] It is striking that the line broadening below −20 °C is indeed most pronounced in the LDPE sample, which has the highest branching.

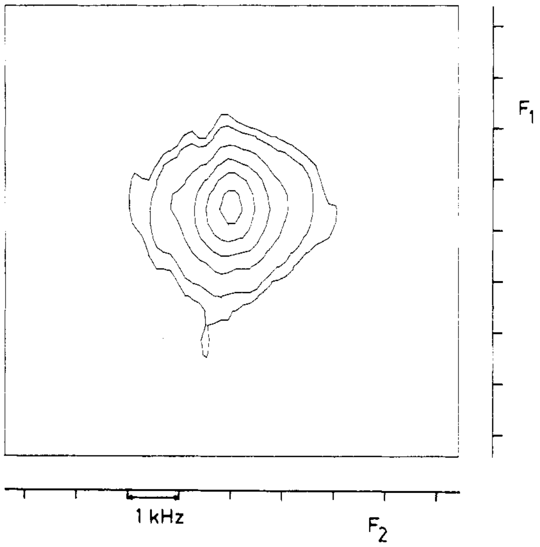

Figure 2. 2D exchange spectrum of ^{129}Xe in polycarbonate. Clearly, xenon samples all local environments in the amorphous polymer within the mixing time of 1 s.

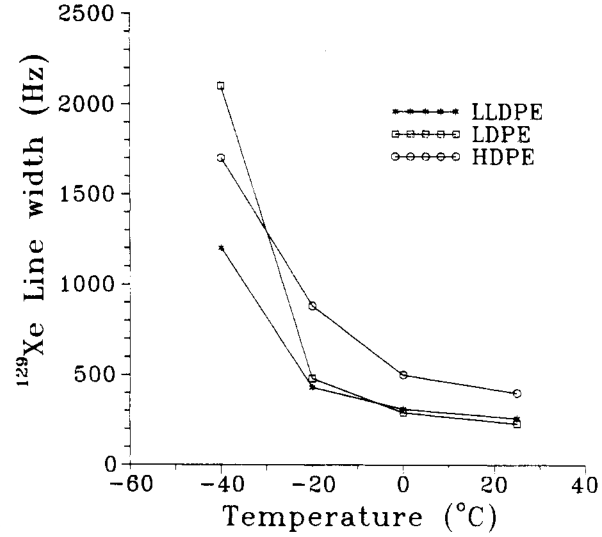

Figure 3. Line width of the xenon resonance at 11.7 T in LLDPE, LDPE, and HDPE as a function of temperature.

An examination of the spectra at −40 °C shows that the resonance consists of two signals from two subregions in the amorphous phase. Again, this is most clearly pronounced for the LDPE sample. Recording this spectrum with and without proton decoupling (Figure 4) shows that xenon experiences a dipolar interaction with the surrounding protons of the polymer chains in one of these regions. There are two possible explanations for this observation: the first is that the spectrum is a reflection of regions in the polymer with a different mobility, e.g., more and less branched regions, so that in the more mobile region xenon–proton dipolar interactions are averaged,

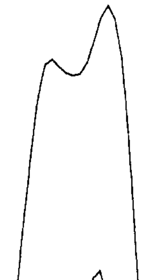

Figure 4. 11.7-T ^{129}Xe spectrum of LDPE, at a temperature of −40 °C with (a) and without (b) proton decoupling.

whereas in the more rigid parts of the sample a net dipolar interaction remains. A second explanation is that in some parts of the sample void spaces are formed, which have a favorable radius for the xenon to be trapped in, according to the model by Ripmeester and Ratcliffe.[6] For xenon trapped in such sites, a bigger xenon–proton interaction with the surrounding polymer is expected than for xenon in larger voids where a xenon atom partitions its time between a free and a sorbed state. More information about this matter might be obtained by performing selective double-resonance experiments. Investigations along these lines are in progress.

In conclusion we can say that ^{129}Xe NMR can yield valuable information about the amorphous phase of solid polymers. For the interpretation of the data several factors have to be taken into account. First, as has been shown for PE, the mobility of the polymer plays an important role; it appears, however, that even above the glass transition temperature different subregions can be observed in the amorphous phase. Another important factor is the xenon diffusion between various sites. If one wants to study the true distribution of void spaces in an amorphous polymer, the presence of microphases in block copolymers, or the compatibility of blends, it is clearly of the utmost importance to have knowledge of the exchange of xenon between various sites. In such cases, magic angle spinning experiments, with or without proton enhancement, at low temperatures seem preferable. The feasibility of such experiments has been demonstrated by Ripmeester et al.[1,5]

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