Xenon Self-Diffusion in Organic Polymers by Pulsed Field Gradient NMR Spectroscopy

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ABSTRACT: Xenon self-diffusion coefficients of commercially available organic polymers have been determined by application of pulsed field gradient (PFG) NMR spectroscopy. Xenon diffusion in the elastomeric terpolymer ethylene−propylene−diene (EPDM) was found to be about 20 times faster than in the more rigid semi-crystalline poly(propylene) (PP). In a polymer blend of both materials consisting of 80% PP and 20% EPDM both diffusion coefficients are in the same range and between the values of the pure materials. As SEM pictures show, this incompatible blend consists of small EPDM domains (1−3 μm) within the PP matrix. The root mean square displacement of xenon within the time interval of the PFG NMR experiment is greater than the domain sizes of EPDM. These results also evidence that xenon in this blend is mainly absorbed in EPDM domains and in the PP matrix near the PP/EPDM interface.

Introduction

In recent years ^{129}Xe NMR spectroscopy has become a powerful technique which was successfully applied to investigate microporous materials like zeolites,[1,2] clathrates,[3,4] and biological substances.[5,6] In comparison to other adsorbates as a NMR probe, the main advantages of xenon are its relative inertness and the large polarizability of its electron cloud, resulting in a large range of chemical shifts in the ^{129}Xe NMR spectra of sorbed xenon. While noncrystalline or semicrystalline organic polymers can also be considered as porous materials a number of reports deal with applications of ^{129}Xe NMR spectroscopy to organic polymers. For example, Kennedy[7] could detect cross-linking effects in a commercial terpolymer using ^{129}Xe NMR spectroscopy. Mansfeld et al.[8] and Schantz et al.[9] investigated polymer blends with ^{129}Xe NMR. Others have studied the glass transition temperature of various polymers by recording ^{129}Xe spectra as a function of temperature.[10,11]

The determination of xenon self-diffusion coefficients allows the calculation of the root mean square displacement in three dimensions $\langle r(t)\rangle$ of xenon in the observed material via the Einstein−Smoluchowski equation[12]

$$\langle r(t)\rangle = \sqrt{6Dt} \tag{1}$$

and so represents a source for information about the structure of porous materials. The xenon self-diffusion in polymers, for instance, reflects the mobility of polymer chains and the xenon diffusion coefficient therefore can be used to characterize polymer materials. From the value of the xenon self-diffusion coefficient in polymer blends domain sizes in polymer blends can be estimated. Until now the xenon self-diffusion coefficients D in organic polymers have been determined for only two systems. Simpson et al.[13] have determined D in polystyrene to be $(1.9 \pm 0.4) \times 10^{-13}$ m^2/s at 25 °C. This value is based on the measurement of spin−lattice relaxation times. Walton et al.[14] reported a value of 4×10^{-11} m^2/s for D at 25 °C in polyisoprene, calculated on the basis of ^{129}Xe NMR line widths.

In this article we present the measurement of xenon self-diffusion coefficients in polymer materials using the *p*ulsed *f*ield *g*radient (PFG) NMR technique. Our special interest lies in the comparison of the Xe diffusion in two polymer materials, semicrystalline poly(propylene) (PP) and the elastomeric terpolymer ethylene−propylene−diene (EPDM), *and* in their blend.

The PFG NMR Technique

While in the past, the isotopic tracer techniques were the methods of choice for monitoring molecular diffusion processes, nowadays the PFG NMR method is the technical mainstay. The advantages of this very elegant way to determine diffussion coefficients, compared to the tracer exchange methods, are well known and described elsewhere.[15] The PFG NMR technique was developed by Stejskal and Tanner in 1965[16] and has found general application in ^{1}H PFG NMR studies of the diffusion of various organic substances in porous materials. As for ^{129}Xe PFG NMR this technique has been used by Heink et al. to measure xenon diffusion coefficients in the zeolites ZSM-5, NaX, and NaCaA.[17]

The standard PFG NMR technique is based on a Hahn-spin-echo pulse sequence (90°−τ−180°−τ), during which two field gradient pulses of strength G and duration δ are applied. The field gradient pulses are arranged to lie between the $\pi/2$ and the π pulse and between the π pulse and the echo acquisition and they are separated by the time interval Δ. Under the influence of these field gradient pulses, any change in position of the observed spins with respect to the field gradient direction during the time interval Δ will lead to an attenuation of the spin-echo intensity. The following relation, derived by Stejskal and Tanner,[16] makes it possible to calculate D from the echo attenuation factor $A(G)/A(G{=}0)$.

$$\ln\left(\frac{A(G)}{A(G=0)}\right) = -\gamma^2\delta^2 D\left(\Delta - \frac{1}{3}\delta\right)G^2 \tag{2}$$

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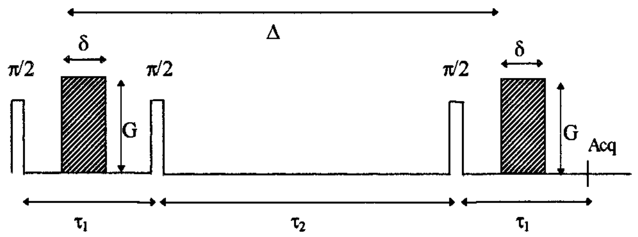

Figure 1. Pulse scheme of the stimulated echo pulsed field gradient technique.

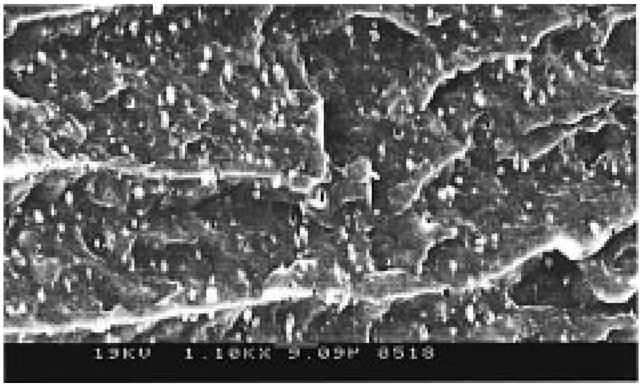

Figure 2. SEM picture of the polymer blend PP/EPDM (80%/20%).

$A(G)$ stands for the echo amplitude in the presence of the field gradient of strength G, and γ denotes the gyromagnetic ratio of the considered nuclei. A plot of $\ln[A(G)/A(G{=}0)]$ vs $-\gamma^2\delta^2\{\Delta - (^1/_3)\delta\}G^2$, varying G, directly yields D by the slope of the resulting curve. A variation of δ or Δ instead of G would also lead to D, but the relatively short spin−spin relaxation times T_2 in ^{129}Xe NMR spectra set too small limits to the variation of these parameters. The short xenon T_2 relaxation times for the polymers we studied, especially for the blend, in the range of 3−8 ms, in combination with moderate field gradients, up to ∼4 T/m, is the reason why we have chosen for the stimulated echo pulse sequence ($90°-\tau_1-90°-\tau_2-90°-\tau_1$, Figure 1), instead of the Hahn echo.

The stimulated echo pulse sequence circumvents the T_2 relaxation time problems by the possibility to extend Δ to much higher values, because during τ_2 only T_1 relaxation takes place.

Experimental Section

Two commercially available polymers were used in our experiments: the polypropylene Vestolen P7000 (Hüls AG, Marl) with a 95 % isotactic structure and the ethylene−propylene−diene terpolymer BUNA AP 437 G (Hüls AG, Marl), containing the diene component 3,5-ethylidene−norbornene. In addition, the blend of these two polymers consisting of 80% PP and 20% EPDM was investigated. It is known that these two polymers form phase-separated blends. The PP builds a matrix in which small EPDM domains are embedded, as evidenced by the SEM picture in Figure 2. The SEM picture also shows some empty pores; these are probably caused by the breaking of the material at liquid nitrogen temperature (that is below the glass transition temperature) during the preparation for the SEM pictures. NMR samples were prepared by placing ca. 2 g of the polymer material into 10 mm pyrex NMR tubes which were then evacuated for several hours. After this a defined amount of xenon was condensed into the tube by cooling it to liquid nitrogen temperature, and the tube was sealed off. The xenon pressure at room temperature was in the range of ∼12 to ∼14 bar.

All experiments were carried out on a Bruker CXP 200 spectrometer by use of a conventional high-power broadband probe head Bruker Z 32v HP, which was modified by us by installing a quadrupole field gradient coil.[17,18] Field gradient pulses were produced by a Bruker Gradient Unit Z 18 B with a maximum current of 17 A, powered by two 12 V Pb/PbO_2 storage cells. Field gradient calibration was performed with the ^{2}H resonances of a D_2O reference sample. The known self-diffusion coefficient of D_2O[19] and the deuterium resonance frequency not far away from the ^{129}Xe resonance frequency permit diffusion measurements and calibration of the field gradient strength without major modifications of the probe. The calibration was then verified by measuring the self-diffusion coefficient of CD_3OD, which was found to be $(2.13 \pm 0.04) \times 10^{-9}$ m^2/s, close to the literature value[19] ($D = 2.11 \times 10^{-9}$ m^2/s). All experiments were made at room temperature, with 6000 FID accumulations for ^{129}Xe in PP, 1000 for EPDM, and 12000 for the PP/EPDM blend and with a maximum field gradient strengh of 4.38 T/m (438 gauss/cm). For each sample, 10 gradient magnitudes were employed, which resulted from 10, nearly linearly increasing coil currents up to 17 A, with constant duration and separation times of the field gradient pulses (see Figure 1). The durations δ (separation times Δ) were 1.2 ms (1.5 s), 0.6 ms (0.35 s), and 0.8 ms (1.2 s) for PP, EPDM, and the PP/EPDM blend, respectively.

To avoid signal attenuation by eddy currents induced by the pulsed gradient fields, the time between the end of the gradient pulse and the subsequent rf pulse or the start of the acquisition was at least 2 ms.

The conventional ^{129}Xe NMR spectra in Figure 3a−c of the three samples described above were recorded with an accumulation number of 10 000 for each spectrum.

Results and Discussion

The ^{129}Xe NMR spectrum of the PP/EPDM blend consists of three resonances (Figure 3c): the peak of free xenon gas, which is used as the reference signal (0 ppm), and the resonances of absorbed xenon in the EPDM domains (∼202 ppm) and in the PP matrix (∼218 ppm). The resonances have the same chemical shift as the ^{129}Xe NMR resonances of the corresponding pure material (Figure 3a,b). The presence of the two signals from absorbed xenon allows the measurement of the xenon diffusion coefficient in both phases of the polymer blend. One distinct difference between the xenon resonances of the polymer blend compared with those of the pure materials is the line broadening in the polymer blend, which is due to the much shorter xenon T_2 relaxation times in the polymer blend. This effect is partly caused by the small domain sizes of the EPDM in the PP matrix, so that Xe atoms can exchange between EPDM domains and the PP matrix.[8] The exchange, however, is not so fast that during the free induction decay the resonance frequency of xenon in EPDM and in PP is averaged. Table 1 and Figure 4 show the results of the xenon self-diffusion measurements. As one would expect, the diffusion in the pure elastomer EPDM is much faster ($D = (78 \pm 1) \times 10^{-12}$ m^2/s) than in the more rigid pure PP material ($D = (3.8 \times 0.2) \times 10^{-12}$ m^2/s). In contrast to the pure components the diffusion coefficients for xenon in the PP/EPDM blend for the PP matrix and for the EPDM domains are of comparable size and in between the values for xenon in EPDM and in PP. As Figure 4 shows the accuracy of the measurement, unfortunately, is lower due to the much shorter xenon T_2 in the blend, but the trend is clear.

This leads to the following two conclusions.

(1) The root-mean-square displacement of the xenon spins during the diffusion time interval Δ of 1.2 s, calculated via eq 1 with the diffusion coefficient of xenon

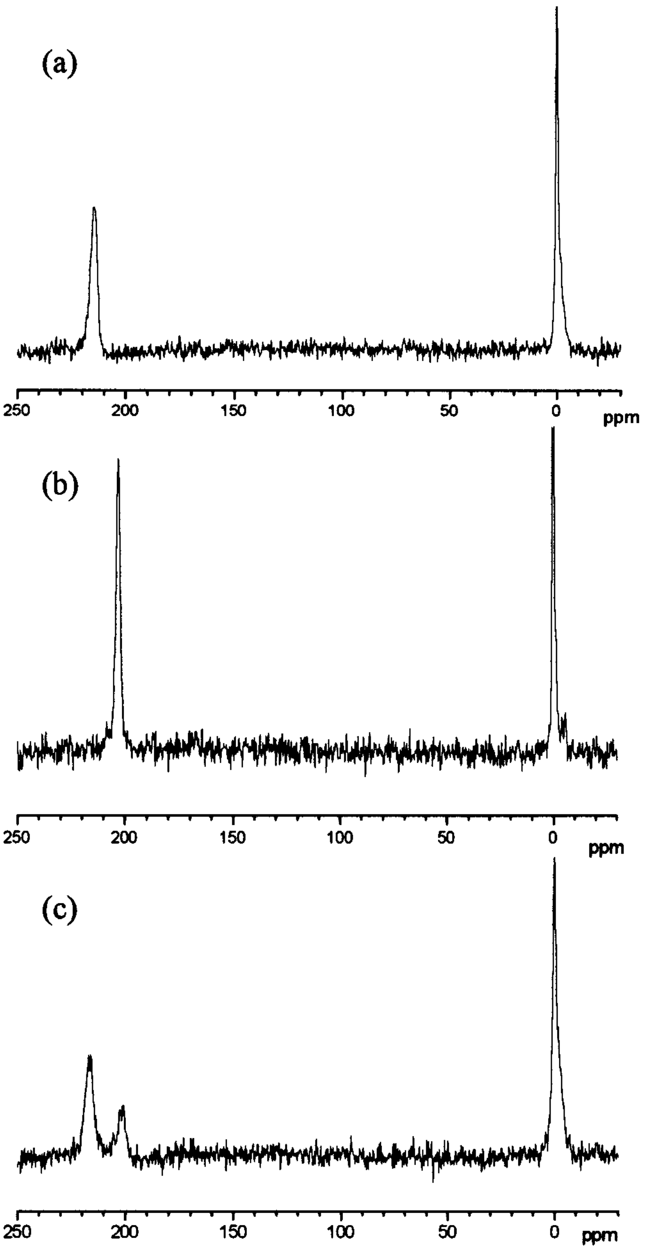

Figure 3. (a) ^{129}Xe NMR spectrum of PP. (b) ^{129}Xe NMR spectrum of EPDM. (c) ^{129}Xe NMR spectrum of the polymer blend PP/EPDM (80%/20%).

Table 1. Xenon Self-Diffusion Coefficients *D* in PP, EPDM, and the Polymer Blend 80%PP/20% EPDM

	D (m^2/s)	
	PP part	EPDM part
PP	$(3.8 \pm 0.2) \times 10^{-12}$	
EPDM		$(78 \pm 1) \times 10^{-12}$
blend	$(8.6 \pm 0.4) \times 10^{-12}$	$(12 \pm 1) \times 10^{-12}$

in EPDM, is ~20 μm. The EPDM domain sizes in the PP matrix are in the range 1−3 μm (see SEM picture, Figure 2). This means that during the time interval Δ, the xenon atoms in EPDM domains can easily cross the PP/EPDM interface. Therefore most xenon atoms, which are in EPDM domains during NMR data acquisition, have been in the PP matrix during the diffusion interval Δ. In the same way, many xenon atoms which are located in the PP matrix during detection must have spent some time in an EPDM domain, while their diffusion constant is higher than that of pure PP. The xenon diffusion coefficients in the blend are time weighed averages of the diffusion coefficient of xenon in EPDM and in PP, as the experimental results show. The xenon exchange between PP and EPDM is, however, too slow to average the two resonance frequencies in the ^{129}Xe spectrum (Figure 3c).

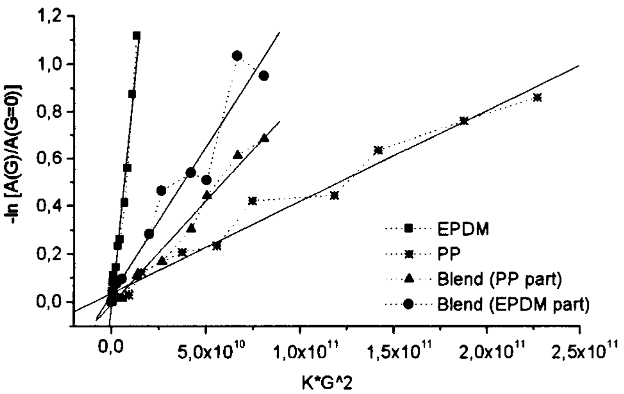

Figure 4. Plot of $-\ln[A(G)/A(G{=}0)]$ vs $\gamma^2\delta^2(\Delta - 1/3\delta)G^2 = KG^2$ for the calculation of the xenon self-diffusion coefficient *D* in EPDM, PP, and the polymer blend PP/EPDM (80%/20%). For values of *D*, see Table 1.

(2) By calculating the root mean square displacement for xenon in PP, using the diffusion coefficient for xenon in PP, we find ~5 μm. The fact that the diffusion coefficient of xenon in the PP matrix in the blend is clearly affected by the presence of the EPDM domains, implies that most of the xenon in the PP matrix is absorbed within ~5 μm of the PP/EPDM interface! This confirms the general belief that Xe is not absorbed in the crystalline regions of the PP matrix but is absorbed in amorphous domains with increased chain mobility and/or increased free volume. Apparently, the amorphous fraction of PP in the blend is mainly found around the EPDM domains.

Since the SEM pictures show also some large empty pores we checked whether the free Xe signal at 0 ppm is partly due to xenon absorbed in these holes. More or less free xenon in large pores could explain the asymmetrical line shape of the resonance at 0 ppm. In that case it is expected that the diffusion coefficient of the free gas peak will show two components, one for the free xenon outside the sample and a slower component for diffusion in the small empty pores in the material. The value for the xenon diffusion coefficient for the free xenon gas is found to be $D = (3.60 \pm 0.18) \times 10^{-7}$ m^2/s, with a good linear correlation in the echo height vs G^2 plot. Apparently, the asymmetrical line shape of the xenon line at 0 ppm in all three spectra of Figure 3 can not be ascribed to some xenon atoms moving freely in the empty pores found in the SEM pictures. Most likely, these pores are caused by the preparation for the SEM experiment and are not present during the NMR experiments.

For comparison we measured *D* for a pure xenon sample under the same conditions. The resulting self-diffusion coefficient was measured to be in the same range, $D = (7.24 \pm 0.2) \times 10^{-7}$ m^2/s, but was still significantly larger than that for the samples with polymers. This deviation and the asymmetrical xenon line shape at 0 ppm is probably due to adsorption of part of the xenon gas atoms at polymer surfaces.

Conclusion

We showed that PFG NMR spectroscopy can be used to measure xenon self-diffusion coefficients in polymer materials. The self-diffusion coefficient of xenon in elastomers like EPDM is about 20 times higher than in the more rigid thermoplast like PP. In the incompatible polymer blend PP/EPDM, the self-diffusion coefficient of xenon in both components are in the same range, because the root-mean-square displacement of the observed xenon spins in our experiments is greater than the EPDM domain size in the PP matrix. The results also prove that xenon in the PP/EPDM blend is mainly absorbed in the EPDM domains and in the PP matrix close (~5 μm) to the PP/EPDM interface.

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