characterized by a repetition distance of the order of 200 Å, a distance that compares well with polyethylene.[11] Changes in solubility and mechanical properties are undoubtly related to this structural modification. The membrane reconstructed at room temperature may be considered to be "a compact nearly dried solution", meaning that only small rearrangements and small reentanglements can occur, not enough to prevent room-temperature dissolution in numerous polar solvents. On the other hand, annealing in the presence of residual additional solvent leads to large structural modifications with entanglements and cross-links preventing dissolution. Although they exhibit similar macroscopic behavior, for instance their insolubility in polar solvents, there are marked structural differences between the as-received Nafion membrane and the membrane reconstructed at high temperature.

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Registry No. Nafion 117, 66796-30-3.

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Nuclear Magnetic Resonance of Xenon Absorbed in Solid Polymers: A Probe of the Amorphous State

The characterization of amorphous regions within solid polymers is important to the understanding of polymer structure and properties. However, there are but a few physical techniques that can be applied to amorphous structure on a microscopic scale. Here we report a technique that uses a small probe molecule contained within the amorphous solid.

The xenon atom is well suited for use as a probe of liquids and noncrystalline solids. It is a small, nonpolar atom, and it is chemically inert under ordinary conditions. It causes minimal disruption of the structure being probed. It has been shown that the xenon NMR spectrum is unusually sensitive to the nature of its immediate environment.[1] Xenon NMR has been used as a probe of simple liquids,[2-4] zeolite surfaces,[5] clathrates,[6] mordenites,[7] and proteins.[8] The NMR spectrum of ^{129}Xe absorbed in poly(vinyl chloride) has been observed.[9] Here we report its use as a probe of amorphous and semicrystalline polymers.

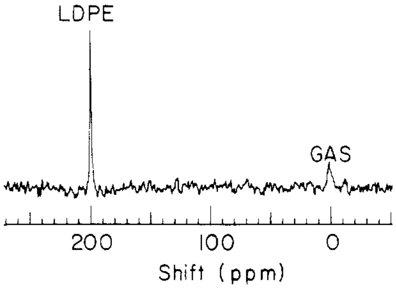

Figure 1. ^{129}Xe spectrum at 24.79 MHz from 8 atm of xenon gas in contact with granulated low-density polyethylene.

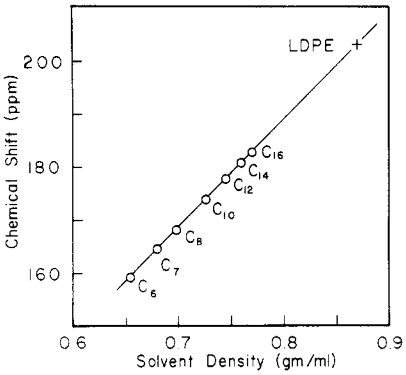

Figure 2. Chemical shifts of ^{129}Xe dissolved in liquid n-alkanes compared with the shift in low-density polyethylene. The shift reference is xenon gas extrapolated to zero pressure.

Linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) were obtained from the laboratory of R. S. Stein. They are characterized as follows: LDPE, $M_w = 286000$, $M_w/M_n = 16$, density of 0.920 gm/cm^3; LLDPE, $M_w = 114000$, $M_w/M_n = 4.5$, density of 0.918 gm/cm^3. Secondary standard poly(ethyl methacrylate) was obtained from Polysciences, Inc. It is characterized by $M_w = 340000$ and $M_w/M_n = 2.7$. The NMR samples were prepared by placing 1 or 2 g of the granulated polymer in a 10-mm NMR tube that had a wall thickness of 1 mm. The tube was attached to a vacuum line, and the sample was thoroughly evacuated. Liquid nitrogen was used to condense in sufficient xenon to produce a gas pressure of ca. 8 atm in the tube at room temperature, and the tube was sealed off under running vacuum.

NMR spectra were obtained on two instruments, a JEOL FX-90Q located at Mount Holyoke College and a Varian XL-300 at the University of Massachusetts NMR Center. Center-band frequencies for the nuclide ^{129}Xe were 24.79 and 82.974 MHz, respectively. Despite the high xenon concentration, acquisition times of 1 h or more are required, because the lines are broad and the relaxation times are long. The higher field of the XL-300 gave no great advantage in this regard, since the lines are broader and the relaxation times longer at the high field.

The ^{129}Xe spectrum of xenon in LDPE is shown in Figure 1. The signal labeled "gas" arises from gaseous xenon which fills the spaces between the polymer granules. This peak has essentially the same chemical shift as pure

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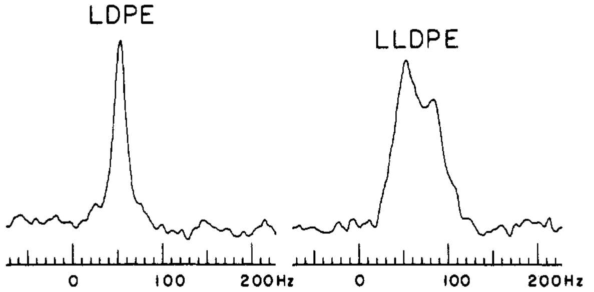

Figure 3. Comparison of the ^{129}Xe signals at 24.79 MHz from xenon absorbed in low-density and linear low-density polyethylenes.

xenon gas at 8 atm, which is ca. 4 ppm downfield from the extrapolated zero-pressure shift.[10]

The LDPE peak is due to xenon contained within the amorphous region of the sample. This assignment is confirmed by the data shown in Figure 2. When xenon is dissolved in a liquid alkane, the resonance is shifted 150–180 ppm downfield from the free gaseous atom.[2] This medium effect is usually treated in terms of a reaction field model, which assumes that spontaneous electric moments arising in the solute induce a reaction field in the solvent which in turn affects the magnetic shielding of the solute.[11] In a very closely related group of solvents, such as the *n*-alkanes, the reaction field, and hence the shift, varies in a simple way with solvent density. In Figure 2 the shift of xenon in a group of *n*-alkanes is plotted vs. density. When the line is extrapolated to the shift of xenon in LDPE, the corresponding density is 0.87 g/cm^3. This agrees well with the value of 0.86, which is usually accepted for the amorphous region of polyethylene. This result shows that the xenon is contained within the amorphous region exclusively.

The shapes of the ^{129}Xe signals from LDPE and LLDPE are shown in Figure 3. The resonances are broad, and the LLDPE peak shows some structure. The line shape appears to arise from a distribution of xenon environments of differing chemical shifts, among which the exchange of xenon is slow on the NMR time scale. This interpretation is supported by the fact that the line widths (in hertz) obtained at 82.972 MHz are ca. 3 times larger than the 24.79-MHz values. The second peak of the LLDPE signal must indicate the presence of two different subregions in the amorphous phase. Minor differences in density or geometry could explain the 1.4 ppm shift. An important consequence of Figure 3 is the fact that the xenon NMR signal is especially sensitive to the amorphous phase structure, a fact which augurs well for its utility as a probe of structure.

Since the xenon chemical shift is sensitive to the density of the surrounding medium, one expects that it will be affected by the glass transition of an amorphous polymer. Poly(ethyl methacrylate) (T_g = 65 °C) was chosen to test this idea. The results are shown in Figures 4 and 5. The chemical shift as a function of temperature for 20 °C on either side of T_g is shown in Figure 4. There is a change in slope at 63 °C, but the break is so small that it could be argued that the data can be represented by a smooth curve over the entire temperature range within the experimental error. Figure 5 shows the behavior of the line width (obtained at 24.79 MHz) over the same temperature range. Here the change in slope at 63 °C is unmistakable. It is likely that the reduced line width at higher temperatures is due to an increase of the rate of chemical exchange of xenon among the various environments within the amorphous phase. As the rate becomes fast with respect to the NMR time scale, the line will become narrow.

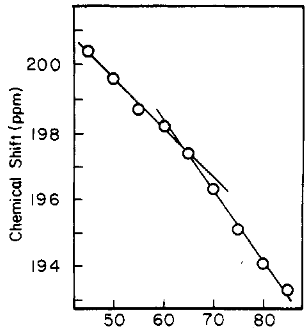

Figure 4. Chemical shift of ^{129}Xe absorbed in poly(ethyl methacrylate) as a function of temperature. The shift reference is xenon gas extrapolated to zero pressure.

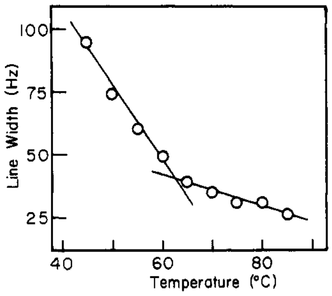

Figure 5. ^{129}Xe line width at 24.79 MHz of xenon absorbed in poly(ethyl methacrylate) as a function of temperature.

According to this model the data in Figure 5 simply reflect the effect of free volume on the exchange rate. On the other hand it is possible that polymer chain motions play a significant role in the xenon line shape. Future experiments at higher frequencies will shed light on this point. These line-width data again demonstrate the sensitivity of the xenon NMR signal to its environment within a solid amorphous structure.

In summary, the NMR spectrum of xenon contained within the amorphous phase of a solid polymer is simple to obtain with standard multinuclear spectrometers, although several hours may be required for signal acquisition. The chemical shift and the line shape are very sensitive to the nature of the surrounding medium, which indicates that xenon NMR has great potential as a probe of solid amorphous structure within organic polymers and other materials.

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Registry No. PE, 9002-88-4; Xe, 7440-63-3; poly(ethyl methacrylate, 9003-42-3.

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Mutual Diffusion in a Compatible Binary Polymer Mixture. Variation with Composition

Recently, considerable theoretical interest has been focused on the dynamics of polymer mixtures.[1-5] For unentangled chains the mutual diffusion coefficient is given by

$$D(\phi) = 2D^0(\phi)|\chi_s(N_A,N_B,\phi) - \chi_F(T,\phi)|\phi(1-\phi) \quad (1)$$

where ϕ is the volume fraction of one component, χ_s and χ_F are the Flory–Huggins interaction parameters at the spinodal and in the homogeneous region, respectively, N_A and N_B are the polymerization indices, and D^0 is the average monomeric diffusivity, which depends on the microscopic Rouse mobilities of the two components and the blend composition. In all theoretical treatments so far, these microscopic Rouse mobilities are assumed to be independent of concentration. If the two materials, however, have quite different glass transition temperature (T_g), this assumption is obviously wrong.[6]

In two recent investigations of the mutual diffusion,[6,7] there were large differences between the mobilities of the pure components as reflectd in the large variation of the T_g with blend composition.[8,9] Since no microscopic theory exists for the average mobility $D^0(\phi)$, the interpretation of the experimental $D(\phi)$ needs careful consideration. In addition, the concentration dependence of the thermodynamic term ($\chi_s - \chi_F$) in eq 1 is important and was ignored in ref. 7. The reported enhancement of the mutual diffusion D in the middle ($\phi = 0.5$) of the composition range according to eq 1 can be true only if the product of D^0 and ($\chi_s - \chi_F$) is approximately independent of concentration. However, this was not the case in the mixture of ref 7. Enhanced mutual diffusivity due to segment interactions was recently reported for polystyrene/poly(phenylene oxide) using forward recoil spectrometry.[10] However, again, to partially compensate for the variation of T_g with blend composition, the $D(\phi)$ was checked at constant $T - T_g$ (ϕ). This procedure was thoroughly examined in a light scattering study on a system of polystyrene/poly(phenylmethylsiloxane).[11]

The present polymer mixture polyethylene oxide (PEO) ($M_n = 600$)/poly(propylene oxide) (PPO) ($M_n = 1025$) with narrow molecular weight distributions in both cases supplied by Riedel de Haen was chosen mainly on account of the composition invariance of the average monomeric mobility D^0 as verified from viscosity measurements. The materials have polymerization indices lower than the entanglement value, and the mixture exhibits convenient upper critical solution temperature (UCST).[12] For these samples, the T_g has reached the asymptotic high molecular weight value[13] and both shear viscosity[13,14] and self-diffusion[14] scale with N and N^{-1}, respectively. Mutual diffusion coefficients were determined by measuring the correlation function of the light scattering intensity at a scattering angle of 90°. The light source was an argon ion laser (Spectra Physics 2020) operating at 488.0 nm with a power of 300 mW. Measurements of the mutual diffusion coefficient were performed in the binary mixture PEO/PPO at two temperatures, 361 and 376 K, and different blend compositions.

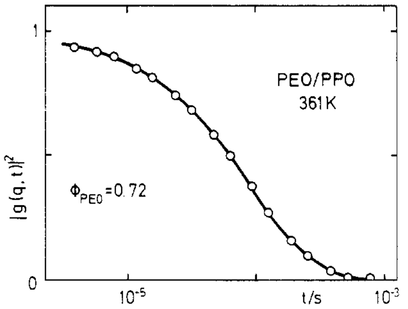

Figure 1. Measured normalized time correlation function of the scattered light intensity due to concentration fluctuations in the polymer mixture PEO/PPO at 361 K and PEO volume fraction $\phi = 0.72$. The solid curve represents a single-exponential fit.

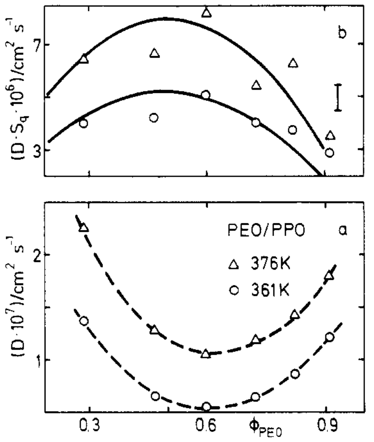

Figure 2. (a) Measured mutual diffusion coefficient D in the compatible mixture PEO/PPO at two temperatures vs. the volume fraction of PEO. The dashed lines are only to guide the eye. (b) This plot is constructed according to eq 1 and takes into account the thermodynamic interactions in the PEO/PPO mixture. This is accomplished by measuring the absolute light scattering intensity S_q due to the concentration fluctuations. The solid lines show the behavior of $D^0\phi(1-\phi)$, where the average monomeric diffusion D^0 amounts to 2.1×10^{-5} cm^2·s^{-1} at 361 K and 3.2×10^{-5} cm^2·s^{-1} at 376 K.

In a polymer blend, besides the scattering of the laser light by thermal density fluctuations, the major part of the total scattered intensity arises from concentration fluctuations, which can be analyzed by using photon correlation spectroscopy.[15] The corresponding time correlation functions were found to have an almost exponential shape with a relaxation rate $\Gamma = Dq^2$ where $1/q$ is the probing wavelength (~1000 Å). An example of the normalized correlation functions $|g(q,t)|^2$ for a volume fraction of PEO $\phi = 0.72$ at 361 K is given in Figure 1, from which Γ can be directly obtained. Alternatively, the static absolute scattered intensity S_q due to the concentration fluctuations is related to the thermodynamic term simply by $2S_q = 1/(\chi_s - \chi_F)$ in the limit $q \rightarrow 0$.[1,2] Thus, information about the thermodynamic driving force and the mutual diffusion coefficient in a compatible polymer blend can be obtained in a light scattering experiment.[11]

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