

## **$^{129}\text{Xe}$ NMR as a probe of the effect of crosslinking on the amorphous phase structure of solid polymers**

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### Summary

$^{129}\text{Xe}$  NMR of xenon adsorbed in a solid EPDM rubber shows the presence of at least four distinct regions in the amorphous phase of this polymer. Changes in the relative amounts of these environments are observed upon crosslinking indicating that changes in the amorphous phase structure of the polymer have occurred.  $^{129}\text{Xe}$  NMR provides a direct probe of the formation of a more condensed amorphous phase of the polymer matrix due to the crosslinking reaction.

### Introduction

The detailed characterization of the amorphous region(s) within solid polymers is a key aspect in the development of a better understanding of polymer structures and properties. In principle the xenon atom should be a good probe of the microscopic heterogeneity of solid polymers. The xenon atom is well suited for use as a probe of solids because it is a small, nonpolar, chemically inert atom, and causes minimal disruption to the structure being probed. Of particular interest and relevance is that the  $^{129}\text{Xe}$  NMR chemical shift is extremely sensitive to the nature of its immediate environment because of its large and polarizable electron cloud. That is, any distortion of this electron cloud is transmitted directly to the Xe nucleus and is manifested as a change in the chemical shift.

It has been long known that the nuclear shielding of  $^{129}\text{Xe}$  is particularly sensitive to density (1,2). The liquid at 244K and the solid at 161K resonate at 161 ppm and 274 ppm downfield respectively from the gas at zero pressure. It has been recently demonstrated (3) that the NMR spectrum of xenon gas that is sorbed in a solid matrix reflects the size and distribution of the void spaces in the solid matrix and thus can be used as a probe of the void spaces and noncrystalline regions of solids. In fact, xenon has now become accepted within the NMR community as a general probe molecule for numerous porous materials such as zeolites (3-15), aluminophosphates (16), aluminas (17), and silicas (18).

There have been three reports (19-21) of Xe NMR studies of xenon adsorbed in polymers. Sefcik et. al. (19) reported the NMR spectrum of Xe adsorbed in poly(vinyl chloride) and showed that the PVC matrix was quite heterogeneous and that the Xe detected a continuous distribution of sites rather than distinct sites. Similar work by Stengle et. al. (20) on low and linear low density poly(ethylene) showed much narrower resonances with chemical shifts indicative of the Xe being exclusively in the amorphous regions of these polymers. Interestingly, a second peak was detected in the spectrum

of the LLDPE indicating the presence of two different subregions in the amorphous phase. Brownstein et. al. (21) reported the observation of Xe in individual microphases within poly(styrene)-poly(isoprene) block copolymers. They suggested that variations in line widths with copolymer molecular weight may be explained by diffusion between the two different phases. These preliminary reports (19-21) clearly demonstrated the potential of Xe as a probe of the amorphous phase structure of solid polymers.

Chemical reactions of solid polymers to form crosslinked network structures are important in defining their material properties and commercial applications. The study of the solid state chemistry of polymers is an area of fundamental importance in understanding the subtleties of structure-property relationships. Changes in the amorphous phase structure may occur during crosslinking reactions that relate to the physical properties of the polymer. However, very little is known about the state of the amorphous regions in crosslinked polymers. In this contribution the first example of the utility of  $^{129}\text{Xe}$  NMR as a probe of the structural changes in the amorphous regions of a solid polymer, introduced by a solid state crosslinking reaction, is presented.

### Experimental

Special NMR tubes were used in this study that are fitted with a rotary Teflon valve (i.e. a J. Young valve (22)) that facilitates connection and disconnection to and from a vacuum line and utilizes a Teflon-to-glass seal to retain the sample in the tube. Samples were prepared by placing 2g of polymer in the NMR tube, attaching the tube to a vacuum line and then thoroughly evacuating the sample. Enough xenon to give a final pressure of approximately 8 atmospheres at room temperature was then transferred to the tube immersed in liquid nitrogen. The tubes were closed off under running vacuum. All samples were allowed to equilibrate at room temperature for a minimum of 16 hours prior to data collection.

The  $^{129}\text{Xe}$  NMR spectra were obtained at 99.637 MHz on a narrow bore Bruker AM-360 NMR spectrometer using a broadbanded 10mm probe. A 10  $\mu\text{s}$  pulse width with a 1 second delay was used for all data acquisition. All chemical shifts are referenced to an external xenon gas standard.

The EPDM rubber investigated in this work was a commercial terpolymer composed of ethylene (66.5 wt. %), propylene (30.6 wt. %), and ethylidene norbornene (2.9 wt. %). The crosslinked material was produced by sulfur curing at 160C for 20 minutes.

### Results and Discussion

The  $^{129}\text{Xe}$  NMR spectrum of xenon adsorbed into a solid EPDM rubber prior to curing (i.e. crosslinking) is shown in Figure 1A. Several different resonances are observed with chemical shifts corresponding to Xe adsorbed into the amorphous phases of the polymer. The observation of at least four distinct peaks indicates the presence of physically distinct environments or domains in the amorphous region of the polymer into which xenon readily adsorbs. The chemical shift of each of these peaks can be

interpreted in terms of the relative size or density of each of these environments. That is, the highest field peak at 198.5 ppm corresponds to the most open void space in the amorphous phase. Similarly the lowest field resonance at 201.0 ppm is attributable to the most condensed void space within the amorphous phase. The intermediate peaks relate to environments that are intermediate in size between these two extremes. The line widths indicate that exchange between these different amorphous domains is slow on the NMR time scale.

Shown in Figure 1B is the  $^{129}\text{Xe}$  NMR spectrum of xenon adsorbed into the same EPDM polymer after it had been crosslinked. This spectrum is dramatically different from the one prior to curing (Figure 1A). These differences are direct evidence of changes in the amorphous phase structure of this polymer resulting from the crosslinking reaction. The most distinct difference is that the peak at 198.5 ppm is no longer present. This is consistent with the removal of the largest amorphous voids during the crosslinking reaction to produce a more condensed or tightly ordered polymer matrix. The removal of this particular amorphous domain may relate to changes in the properties of the polymer such as loss of solubility. The relative intensity of the other peaks also changes with crosslinking which reflects a change in the population of these environments.

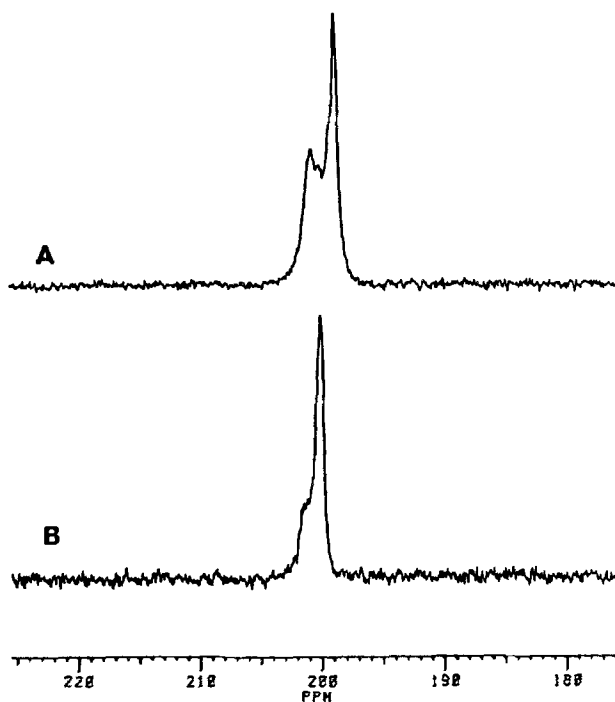


Figure 1.  $^{129}\text{Xe}$  NMR spectra of xenon adsorbed in solid EPDM: (A) before, and (B) after curing.

In conclusion, the  $^{129}\text{Xe}$  NMR experiments described here on EPDM definitively show that there are at least four distinct amorphous regions in the polymer before crosslinking. Spectral changes observed in the crosslinked polymer reflect changes in the relative population of these environments introduced by the crosslinking reaction. These observed changes directly relate to the more condensed, tightly packed polymer matrix that results from the crosslinking reaction. This work clearly demonstrates the potential of  $^{129}\text{Xe}$  NMR techniques to probe and monitor changes in the amorphous phase structure of polymers that may result from solid state reactions such as crosslinking, derivatization, and degradation. Further work is underway in the application of these techniques to defining relationships between amorphous phase structure and polymer properties.

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22. These tubes are commercially available from Wilmad Glass.