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Characterization of Aging in Organic Materials on Atomic-, Meso- and Macro-Length Scales by ^{13}C NMR Spectroscopy

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A fundamental understanding of aging in an organic material requires that we understand how aging affects the chemical structure of a material, and how these chemical changes are related to the material's macroscopic properties. This level of understanding is usually achieved by examining the material on a variety of length scales ranging from atomic to meso-scale to macroscopic. We are developing and applying several ^{13}C nuclear magnetic resonance (NMR) spectroscopy experiments to characterize the aging process of organic materials over a broad range of length scales. Examples of studies which range from atomic to macroscopic will be presented.

I. Chemical Structure by Isotopic Labeling

NMR spectroscopy has traditionally been used to examine the chemical structure of materials. The primary difficulty with the study of aging by NMR spectroscopy is that aging may be controlled by very small amounts of chemical change. We are preparing selectively labeled ^{13}C polymers in order to increase the selectivity and sensitivity of ^{13}C NMR spectroscopy to chemical changes. Preparation of enriched compounds increases the signal-to-noise ratio by nearly two orders of magnitude and reduces the experimental time for a constant signal-to-noise experiment by nearly four orders of magnitude. In addition, the polymer can be selectively enriched so that the enriched functional group serves as a "tag" that can be followed throughout the aging process. Figure 1 shows the two enriched polymers that have been prepared and a comparison of the solid-state magic angle spinning (MAS) ^{13}C NMR spectra of unlabeled and α-^{13}C labeled polystyrene. The spectra confirm that both selectivity and a 100-fold enhancement in sensitivity can be realized.

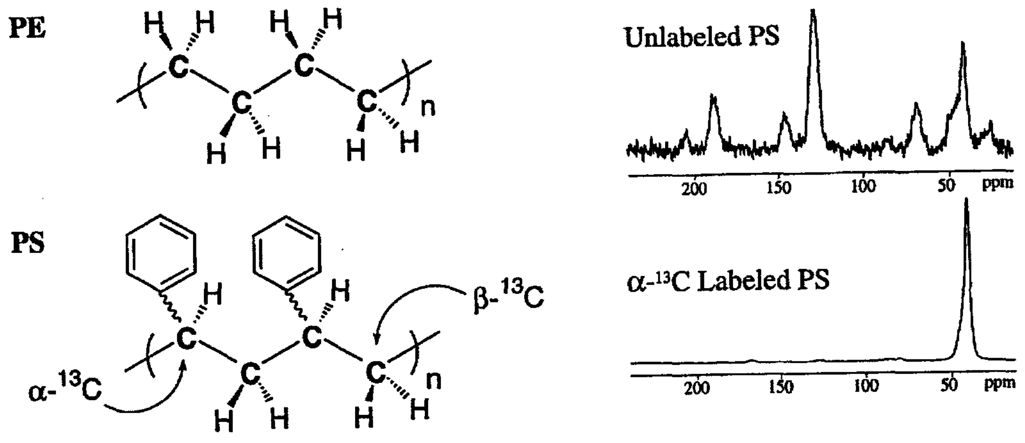

Figure 1. Fully enriched ^{13}C polyethylene (PE) and selectively α– and β-^{13}C enriched polystyrenes (PS) have been prepared. The solid-state MAS ^{13}C NMR spectrum of the unlabeled polystyrene consists of several resonances from the various aromatic carbons as well as resonances from both the α and β aliphatic carbons. The NMR spectrum of the α-^{13}C labeled polystyrene consists of predominately of the α aliphatic resonance.

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II. Meso-Scale Structure in Partially Crystalline Polymers

The meso-scale structure of a polymer is often an important link between the polymer's chemical composition and macroscopic properties. The thermal history of a polymer can also affect its meso-scale structure and hence its properties. The importance of a polymer's meso-scale structure is illustrated by the aging of Dekoron rubber, a partially crystalline ethylene-propylene copolymer. When Dekoron undergoes aging by radiation exposure at 23°C, its gel fraction decreases from 0.7 to 0.0. When the material is annealed at 140°C for 24 hours, the gel fraction recovers to 0.7. The recovery has been termed the "Lazarus" effect. We have been unable to observe chemical changes which provide insight into the recovery. During aging a minor resonance corresponding to vinyl groups disappears; however, no chemical changes are detected during the annealing process.

We are able to observe substantial changes in the material's meso-scale structure during both the aging and annealing steps. Figure 2 shows the ^{13}C NMR spectrum of the (a) unaged, (b) 23°C aged, and (c) 23°C aged and annealed material. The experiments were conducted using parameters which provide quantitative spectra. The spectrum of the unaged sample shows that the polyethylene chain has a crystalline to amorphous ratio of 1.1. After aging, the crystalline to amorphous ratio is equal to 1.9. Radiation has caused chain scission and these shorter chains are able to rearrange and crystallize. The crystalline to amorphous ratio decreases to 1.3 after annealing. Evidently, annealing above the crystalline melting point has reintroduced crosslinking into the system. The crosslinking causes both an increase in gel fraction and a decrease in crystallinity. Thus, the meso-scale structure is a sensitive probe of changes occurring in the chemistry of the polymer backbone. Ultimately we would like to use the increased sensitivity provided by the isotopically labeled polymers discussed in the previous section to observe the polymer backbone and to study the relationship between the chemical and crystallinity changes occurring during both aging and annealing processes.

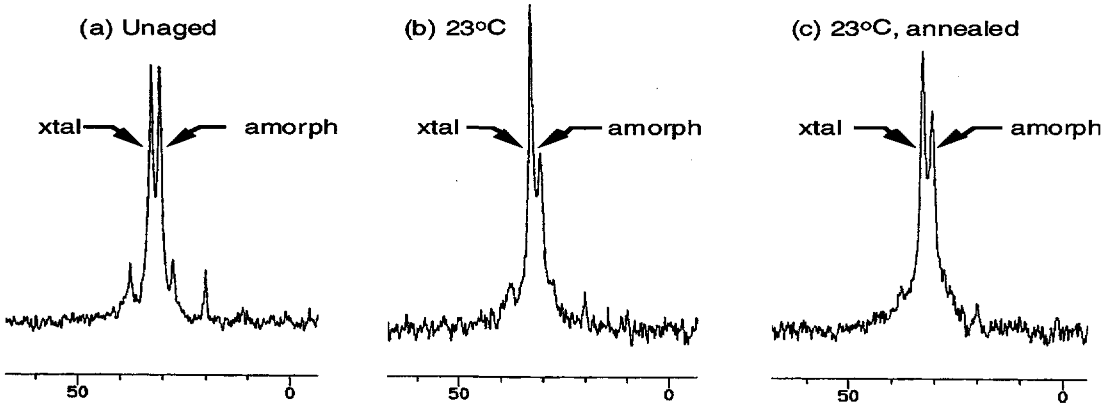

Figure 2. The ^{13}C NMR spectra of (a) Dekoron unaged, (b) Dekoron exposed to 730 kGy at 23°C over 144 days, and (c) sample b after annealing. The resonances at 32.5 and 30.3 ppm correspond to the crystalline (xtal) and amorphous fractions of the polyethylene chain segments, respectively.

III. A Molecular Probe of Young's Modulus

The Young's modulus of a viscoelastic material is an important parameter used to describe the material's mechanical properties. Unfortunately, in many instances, the size or physical form of a sample prohibits the measurement of its modulus by traditional methods. Moreover, many materials consist of two or more microscopic phases or components, and conventional approaches only measure the overall modulus. We are using cross-polarization relaxation experiments to estimate the modulus of a variety of organic materials.

Parker *et al* [1] have shown that both the cross-polarization relaxation time and the Young's modulus of a viscoelastic material are related to the mean molecular reorientation time and thus are related to each other. The reported correlation successfully described polymers with various backbone structures, with and without plasticizers, with both single and multiphase components, and at two observation temperatures. The NMR cross polarization experiment is unique in that it measures the individual responses of chemically distinct molecular units as well as the individual responses of distinct phases such as the crystalline and amorphous phases of partially crystalline polymers.

Figure 3 shows the response of the ^{13}C magnetization for a butadiene/natural rubber copolymer during an NMR cross-polarization experiment. The aged sample had been stored for 44 days in an ambient atmosphere at 110°C. The initial portions of the response curves were fit with a simple exponential function with time constants, T_{cp}, of 0.42 and 0.12 ms for the unaged and aged samples respectively. Parker *et al* have shown that the Young's modulus is proportional to $(1/T_{cp})^2$, therefore the NMR measurements predict that the modulus of the aged sample is 12 times greater than that of the unaged sample. Measurements using a modulus profiler [2] also give a factor of 12. Although this quantitative agreement may be somewhat fortuitous considering the nature of the experiment, the results clearly demonstrate the sensitivity of the cross-polarization experiment to material aging. No signs of chemical changes were visible in the ^{13}C NMR spectrum of the aged sample.

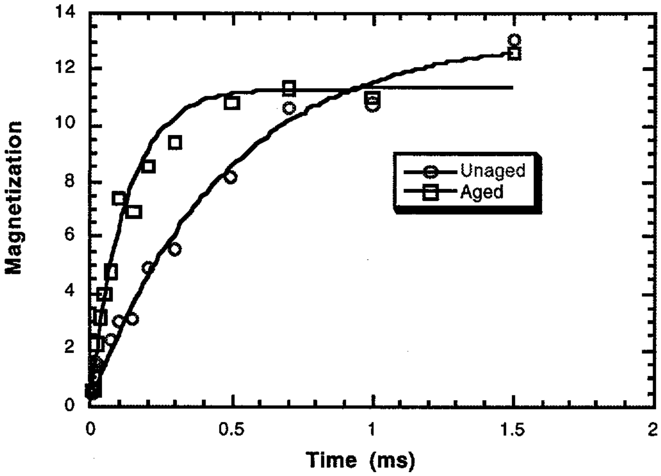

Figure 1. The ^{13}C magnetization response for an unaged and aged sample of butadiene/natural rubber copolymer during a cross-polarization experiment.

REFERENCES

[1] A. A. Parker, J. J. Marcinko, P. L. Rinaldi, D. P. Hedrick, W. M. Ritchey, J. Appl. Polym. Sci., **48**, 677 (1993).
[2] K. T. Gillen, R. L Clough and C. A. Quintana, Polym. Deg. Stab., **17**, 31 (1987).

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