SAND2000-2890J

INVESTIGATION OF THERMAL AND γ-IRRADIATED HYDROLYSIS IN POLYMERS USING ^{17}O NMR

Todd M. Alam

Department of Organic Materials
Sandia National Laboratories
Org. 1811, MS 0888
Albuquerque, NM 87185-0888

Introduction

Understanding polymer aging and degradation is crucial for accurate prediction of polymer lifetime, durability, and reliability. The elucidation of the chemical and physical mechanisms at the molecular level leading to polymer degradation is an important objective in achieving this goal. Nuclear magnetic resonance (NMR) spectroscopy continues to be a powerful tool for the elucidation of aging mechanisms at the molecular level, as well as providing a method for monitoring of material aging. This laboratory has recently reported a series of ^{17}O NMR investigations of degradation mechanisms in thermally aged and oxidatively-irradiated polymer systems.[1-3] In this paper we will discuss the use of ^{17}O NMR spectroscopy to probe the hydrolytic degradation of several important materials including the polyester urethane Estane® 5703, and the silica-filled and unfilled polydimethyl-polydiphenylsiloxane (PDMS/PDPS) copolymer.

Experimental

Materials. The polyester urethane was commercially obtained Estane 5703® (B. F. Goodrich Co., Charlotte, NC). The Estane is composed of hard segments based on 4,4'-diphenylmethane diisocyanate and soft segment based on adipic acid and a 1,4 butanediol chain extender. The Estane 5703® material was utilized as obtained without further processing.

The siloxane material was a random block copolymer consisting of dimethyl (DMS), diphenyl (DPS), and methyl vinyl (MVS) siloxane monomer units. In the base rubber the percentage of each monomer unit was 90.7 wt. % DMS, 9.0 wt. % DPS, and 0.3 wt. % MVS (Nusil Corp., Carpenteria, CA) This material will be referred to as the PDMS/PDPS copolymer through the rest of the discussion. For the filled siloxane samples the copolymer was compounded with silica by milling a mixture of 21.6 wt. % fumed silica (Cab-o-Sil M7D, Cabot Corp., Tuscola, IL.), 4.0 wt.% precipitated silica (HiSil 233, PPG Industries Inc., Pittsburgh, Pa.) and 6.8 wt.% ethoxy-endblocked siloxane processing aid (Y1587, Union Carbide Corp., Danbury, CT.). After bin aging for 3 weeks at room temperature, both the filled and unfilled siloxane polymer gums were cross-linked with a thermally activated peroxide curing agent.

Hydrolysis Aging. The samples were aged by placing appropriate weights of these materials above a saturated K_2SO_4/H_2O salt solution inside a sealed ampoules. Isotopically labeled (47.3% ^{17}O) $H_2{}^{17}O$ water (Isotec, Miamisburg, OH) was used in the preparation of these solutions. The saturated salt solution provided a constant relative humidity (RH) atmosphere for the aging of the polymer samples. The thermal hydrolysis of the estane was accomplished by placing the ampoule in ovens at 50°C or 65 °C for 1-475 days. The γ-irradiated hydrolysis of the PDMS/PDPS copolymer was accomplished by irradiating the sample at 27 °C for up to 14.5 days in a ^{60}Co-facility, at a dose rate of 58 KRad/h.

NMR Measurements. The solution ^{17}O NMR spectra were obtained at a resonant frequency of 54.3 MHz on a Bruker DRX400 spectrometer using a 5 mm broad band probe. Spectra were obtained using 16K to 128K scans, a 10 µs $\pi/2$ pulse, and a 500 ms recycle delay. It was found that the 500 ms delay was sufficient for complete spin-lattice relaxation in the samples. A standard single pulse Bloch decay sequence using composite pulse ^{1}H decoupling. The ^{17}O NMR spectra were referenced to natural abundance $H_2{}^{17}O$ ($\delta = 0.0$ ppm) at room temperature. For all of the experiments described, approximately 20 - 30 mg of thermally hydrolyzed estane or γ-irradiated hydrolyzed PDMS/PDPS copolymer were dissolved in 750 µl of DMSO-d_6 or methylcyclohexane, respectively. For the PDMS/PDPS copolymer the samples were dried in a N_2 environment prior to dissolving in solvent to eliminate the water resonance which has a chemical shift near the resonance of the silanol species. It has been shown that by reducing the molecular correlation time through the use of elevated temperatures, the observed ^{17}O NMR line width in the aged polymer samples can be greatly reduced.[1] The ^{17}O NMR spectra reported in this paper were therefore all obtained at elevated temperatures, with the spectra for both estane and the PDMS/PDPS copolymer being recorded at 75 °C.

Results and Discussion

^{17}O NMR of Hydrolyzed Polymers. Due to the low natural abundance of the ^{17}O isotope (0.037%), the use of isotopic enrichment is required. The need to introduce the ^{17}O label during the aging process can be used to an advantage since the observed spectra will only contain signal from the newly formed degradation products. By careful introduction of the enriched isotope, ^{17}O NMR analysis provides a method to clearly isolate the degradation products, as well as selectively investigate a portion of a overall complex degradation pathway. For example, by introducing labeled water during the hydrolytic aging of polymers, the resulting hydrolysis products are directly observed.

$$\text{Polymer} \xrightarrow[\Delta \text{ or } \gamma]{H_2{}^{17}O(l)} {}^{17}\text{O Labeled Hydrolysis Products}$$

The ability to observe only oxygen labeled degradation species without background signal is shown in the hydrolysis studies presented below. Selective identification of the hydrolysis species formed during theradiolytic hydrolysis of materials (without interference from other interfering degradation species) is also possible using this method, and is demonstrated in the analysis of γ-irradiated hydrolysis of the PDMS/PDPS copolymer.

Thermal Hydrolysis of Estane 5703®. Figure 1 shows the solution ^{17}O NMR spectra for estane aged under 98% RH at 65 °C as a function of aging time. Several different ^{17}O containing species are clearly observed in these spectra.

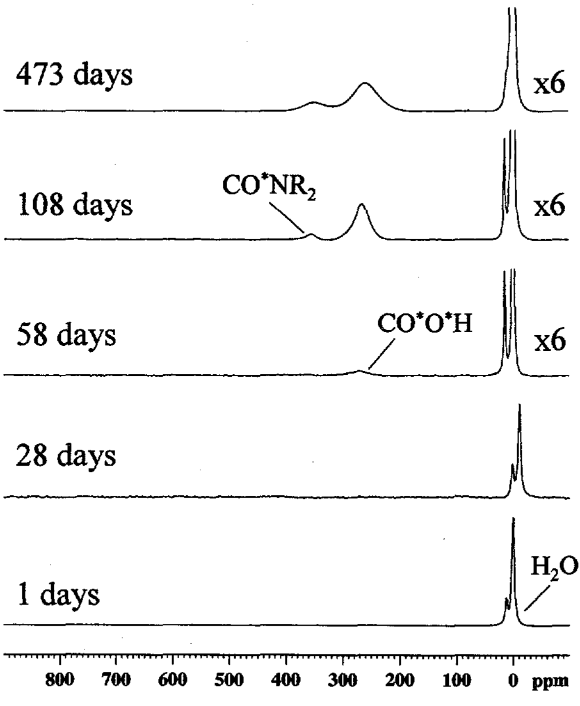

Figure 1. Solution ^{17}O NMR spectra for hydrolyzed Estane 5703® as a function of time. The upper spectra are scaled to allow the newly formed degradation species to be visible.

At short aging times two distinct resonances forH_2O^{17} are seen at $\delta = +1$ and $+ 15$ ppm, and result from water species with distinctly different environments absorbed into the swollen polymer. The use of ^{17}O NMR to directly investigate different water environments has been reported for mixtures of hydrophobic solvent-water mixtures[4,5] or water-petroleum systems.[6]

Carboxylic acid degradation species at $\delta = + 270$ ppm become evident in the ^{17}O NMR spectra at 58 days, and continue to increase with additional hydrolysis aging. These carboxylic acids are formed from the hydrolysis of the ester linkage in Estane. Additional degradation products are observed at 108 days with the appearance of an amide or acetanilide resonance at $\delta = + 360$ ppm. Whether these amide or acetanilide degradation species results directly from the cleavage of the urethane linkage or is the result of a series of secondary degradation reactions is yet to be determined. Extensive aging (473 days) does not reveal the formation of any additional degradation species (top of **Figure 1**). No resonances corresponding to ester contaiing degradation species is observed. Analysis of Estane 5703®hydrolytic degradation at 50 °C (which is below the phase transition of the material) reveals a similar labeled degradation product distribution, but the appearance of the oxygen-containing degradation species occurs at a much longer time scale.

γ-Irradiated Hydrolysis of PDMS/PDPS Copolymer. The solution ^{17}O NMR spectra of the PDMS/PDPS copolymer which was radiolytically hydrolyzed at 27 °C is shown in **Figure 2**, for both the filled and unfilled siloxane material.

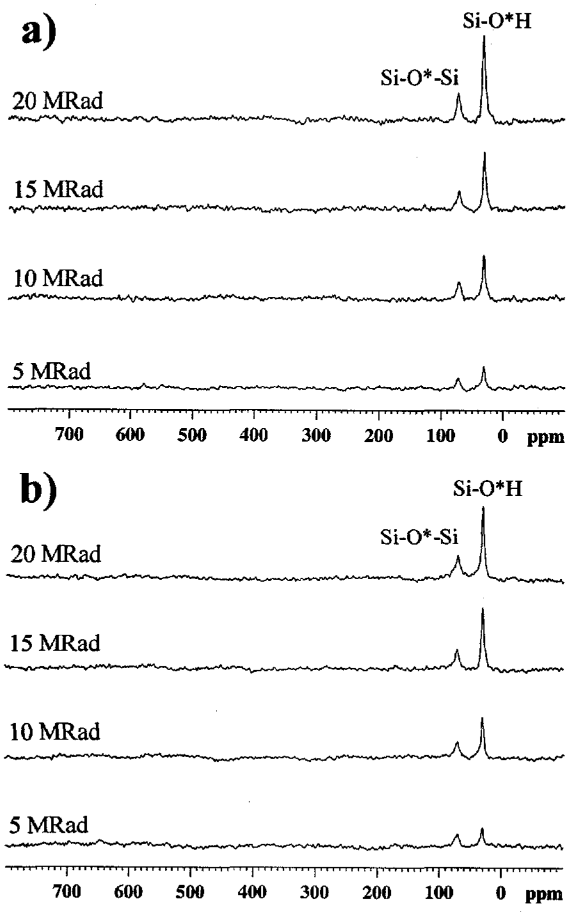

Figure 2. The solution ^{17}O NMR of γ-irradiated hydrolysis of the PDMS/PDPS copolymer as a function of total dose amount for the a) unfilled and b) silica filled rubber.

Two resolved resonances are observed at $\delta = +72$ ppm and $+31$ ppm, corresponding to oxygens in siloxane linkages andsilanols, respectively. The formation of siloxane linkages during the radiolytic hydrolysis is consistent with a back-biting mechanism involving unreacted terminal silanols. The results shown in **Figure 2** reveal that for both the filled and unfilled siloxane rubber the degradation products observed are the same, with no effect of the silica filler. A small difference in the relative concentration of thesilanol and siloxane linkage products in the unfilled and filled material was observed at low radiation dose. At higher total dose amounts the effect of the filler on the differences in relative concentration vanishes.

Conclusions

The use of ^{17}O NMR to investigate hydrolytic aging in polymer systems has been presented. The experiments show that a variety of different degradation products can be observed depending on the nature of the material investigated. Using ^{17}O NMR the relative concentration of the oxygen-containing degradation species can be measure directly from the observed spectrum. These ^{17}O NMR investigations demonstrate that for Estane 5703® that additional degradation products beside the predicted ester cleavage are observed at long exposure times. The results from the PDMS/PDPS copolymer radioyltic hydrolysis demonstrate that the incorporation of filler has only a small effect on the hydrolysis mechanism. In addition these ^{17}O NMR results reveal that new Si-O-Si linkages are formed during the aging process.

These investigations demonstrate the potential of using ^{17}O NMR spectroscopy to probe hydrolytic degradation in polymer systems. By utilizing isotropically labeled degradation experiments the ^{17}O NMR spectra allow for the identification and quantification of non-volatile hydrolysis products unencumbered by background signals from the unaged material. The use of ^{17}O NMR to probe degradation of polymer systems under a variety of different environmental conditions is presently being pursued.

Acknowledgements. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

References

(1) Alam, T. M.; Celina, M.; Wheeler, D. R.; Assink, R. A.; Clough, R. L.; Gillen, K. T. *Polymer News* **1999**, *24*, 186-191.
(2) Alam, T. M.; Celina, M.; Assink, R. A.; Clough, R. L.; Gillen, K. T.; Wheeler, D. R. *Macromolecules* **2000**, *33*, 1181-1190.
(3) Alam, T. M.; Celina, M.; Assink, R. A.; Clough, R. L.; Gillen, K. T. *Rad. Phys. Chem.* **2000**, *59*, (In Press).
(4) Kusanagi, H. *Polymer Journal* **1996**, *28*, 825-826.
(5) Kusanagi, H. *Chem. Letters* **1996**, 41-42.
(6) Dolgopolova, A. V.; Kushnarev, D. F.; Khva, K. E.; Kalabin, G. A.; Schmidt, F. K. *Petroleum Chemistry* **1996**, *36*, 373-377.