Probing Oxidative Degradation in Polymers Using ^{17}O NMR Spectroscopy[†]

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Understanding the mechanism of oxidative degradation remains an important goal in being able to predict the aging process in polymer materials. Nuclear magnetic resonance (NMR) spectroscopy has previously been utilized to investigate polymer degradation, including both proton (^{1}H) and carbon (^{13}C) studies. These previous NMR studies, as well as other spectroscopic investigations, are complicated by the almost overwhelming signal arising from the native undegraded polymer. This makes the identification and quantification of degradation species at small concentrations difficult.

In this note we discuss recent investigation into the use of oxygen ([17]O) NMR spectroscopy to probe the oxidative degradation processes in polymers at a molecular level. Due to the low natural abundance (0.037%) and a nuclear spin of I = 5/2 possessing an appreciable quadrupolar moment, the use of ^{17}O NMR in polymer investigations has been limited. By utilizing synthetically enriched oxygen gas during the accelerated aging process, both the difficulties of low natural abundance and background interference signals are eliminated. For enriched samples ^{17}O NMR spectra now provide a unique probe since all of the observed NMR resonances are the direct result of oxidative degradation.

Oxidative Degradation

The oxidative aging of polymers is expected to produce a wide range of degradation species. For example, a series of possible degradation mechanisms in natural polyisoprene (1) via hydroperoxide (2) formation is presented in Fig. 1.
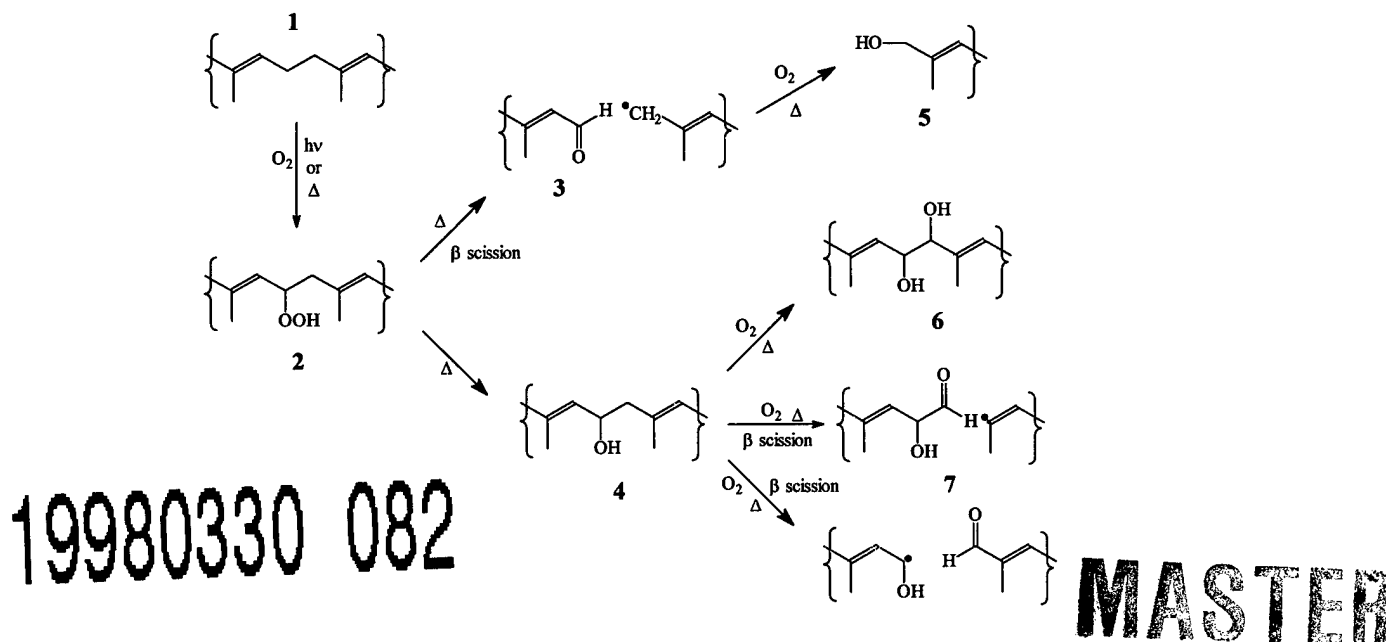

Figure 1. Possible oxidative degradation mechanism in polyisoprene rubber.

DISCLAIMER

A variety of degradation species are observed including aldehydes (**3**), secondary (2°) alcohols (**4**), primary (1°) alcohols (**5**), diols or dihydroxy species (**6**), and γ-hydroxy substituted aldehydes (**7**). The ability to identify and quantify the production of these different degradation species is critical in understanding the mechanisms occurring during the aging process. The solution ^{17}O NMR spectra for polyisoprene rubber aged 59 days at 100°C (1.8% O_2 incorporation by weight) is shown in Fig. 2a. Resonances over a wide range of chemical shifts are observed, and can be quickly assigned to different oxygen functionalities.
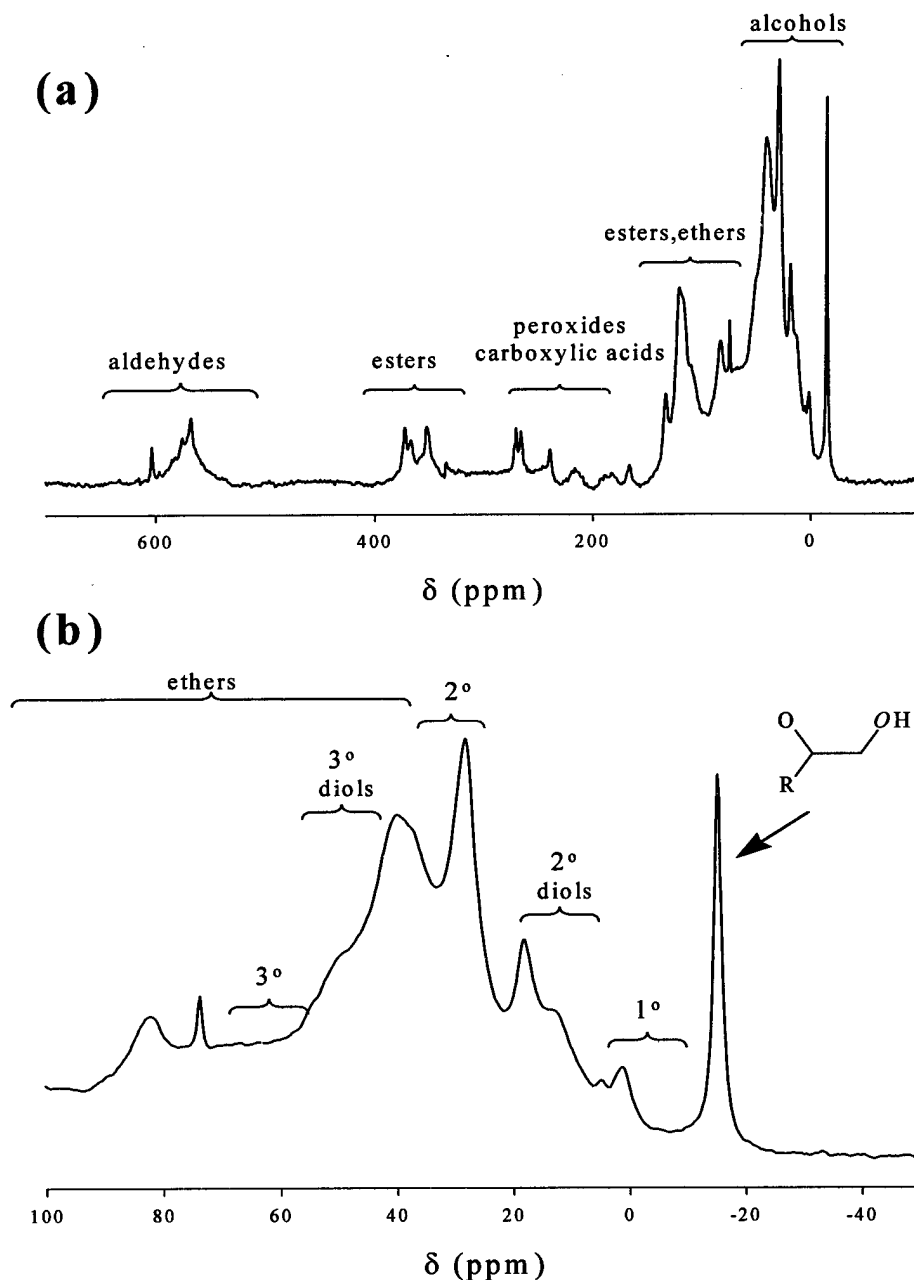

Figure 2. Solution ^{17}O NMR spectra of aged polyisoprene 59 days. 100° C at 250 Torr of 85% enriched $^{17}O_2$ gas: (a) full NMR spectra, (b) expanded region of alcohol resonances.
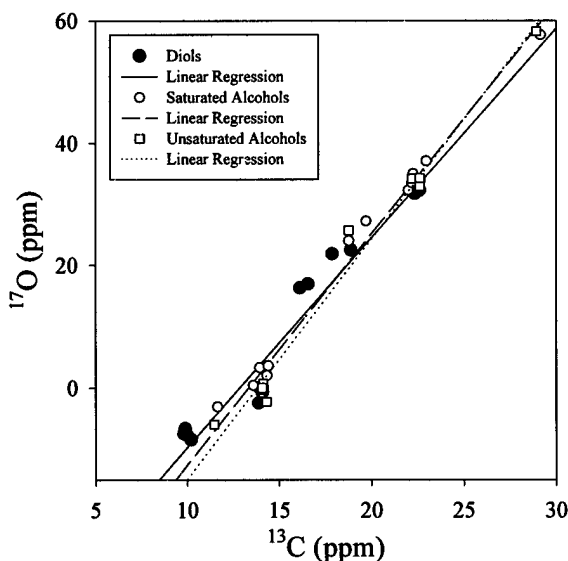
The ^{17}O NMR resonances observed between +600 and +550 ppm can be assigned to the oxygen in aldehydes (3 and 7). The resonances between +400 and +300 ppm result from carbonyl resonances in esters and lactones. The observation of these ester and lactone resonances in Fig. 2a immediately indicate that the oxidation mechanism outline in Fig.1 is incomplete since the production of these is not predicted. The [17]O resonances between +280 and +250 ppm can be associated with alkyl hydrogen peroxides (2), peroxides, and carboxylic acids. The observation of ^{17}O NMR resonances between +210 and +100 ppm result from ester functionalities, and again show the mechanisms in Fig. 1 are incomplete. Saturated and unsaturated alcohols (4 and 5), including diols (6) resonate between +80 and -30 ppm. It is clear from Fig. 2a that a variety of different oxygen containing species are produced during the oxidative aging of polyisoprene, including major concentrations of alcohol containing species.

Identification of Alcohol Degradation Species

Figure 2b shows an expanded plot of the ^{17}O NMR resonances corresponding to alcohol degradation species, allowing detailed information about the different types of alcohols present to be easily assessed. Unlike infrared (IR) spectroscopy where individual type of alcohols cannot be easily distinguished (even using derivatization), distinct chemical shift ranges are present in the ^{17}O NMR spectra for different classes of alcohols to be identified. Inspection of Fig. 2b clearly show that both primary (1°) and secondary (2°) alcohols are readily formed during the aging of polyisoprene. In addition, the presence of the major diol resonance at (~ -14 ppm) reveals that hydroperoxides readily form on adjacent carbons within the polymer.

A major hurdle in the use of ^{17}O NMR has been the prediction of chemical shifts for different species. While there exist a large data base of ^{13}C NMR chemical shifts, as well as reliable relationships between ^{13}C chemical shifts and molecular structure, there is not an equivalent knowledge base for ^{17}O NMR. In Fig. 3 we demonstrate that a linear relationship between the [17]O chemical shift in alcohols (ROH) and the ^{13}C chemical shift of the methyl group in the corresponding alkyl species (RCH3) is observed. This correlation allows us to use the ^{13}C NMR data and prediction programs to predict ^{17}O NMR chemical shifts for different alcohol species. Investigations into the correlations for other functional groups are presently being pursued. This work demonstrates the applicability of ^{17}O NMR in the investigation of polymer aging. We have recently reported investigations for a variety of polymer systems including polypropylene, nitrile rubber and EPDM.[1]

Figure 3. Correlation between the ^{17}O NMR chemical shift of alcohols (ROH) and the ^{13}C NMR shift of the corresponding methyl group in RCH3

References

1. T. M. Alam, M. Celina, R. A. Assink, K. T. Gillen and R. L. Clough *Polymer Preprints* **38**, 784 (1997).

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