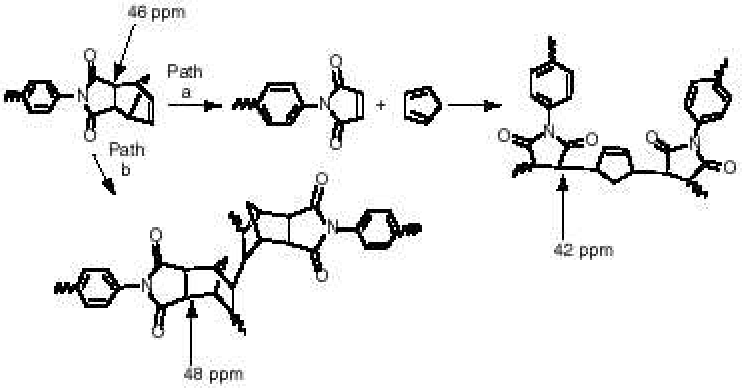
Carbon-13 Labeling Used to Probe Cure and Degradation Reactions of High-Temperature Polymers

High-temperature, crosslinked polyimides are typically insoluble, intractible materials. Consequently, in these systems it has been difficult to follow high-temperature curing or long-term degradation reactions on a molecular level. Selective labeling of the polymers with carbon-13, coupled with solid nuclear magnetic resonance spectrometry (NMR), enables these reactions to be followed (ref. 1). We successfully employed this technique to provide insight into both curing and degradation reactions of PMR-15, a polymer matrix resin used extensively in aircraft engine applications (refs. 2 and 3).

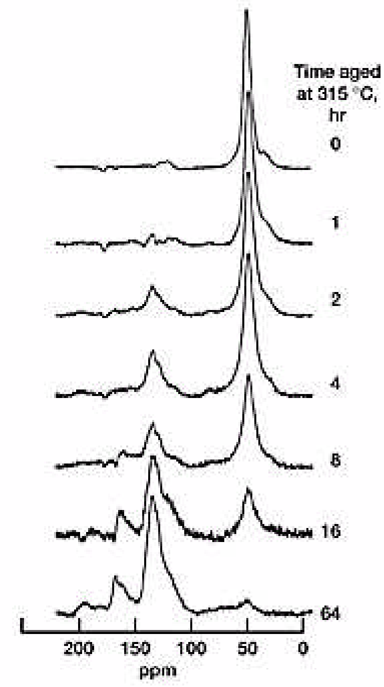


Possible crosslinking pathways for the endcap with the carbon-13 chemical shifts of labeled carbons predicted from model compounds.

PMR-15 is prepared via a two-step approach involving the initial formation of an endcapped prepolymer followed by crosslinking through the endcaps, producing a void-free network. Though the polymer has been studied extensively for more than 20 years, the nature of the crosslinking step has not been well-understood (see the preceding figure). Originally, it was thought that crosslinking occurred through cleavage of the endcap, followed by copolymerization, path a (ref. 4). Later, others suggested that the endcap simply homopolymerized through the double bond, path b (ref. 5). Solid nuclear magnetic resonance of selectively carbon-13 labeled endcap allowed researchers at the NASA Lewis Research Center to unambiguously distinguish between the two pathways (ref. 6).

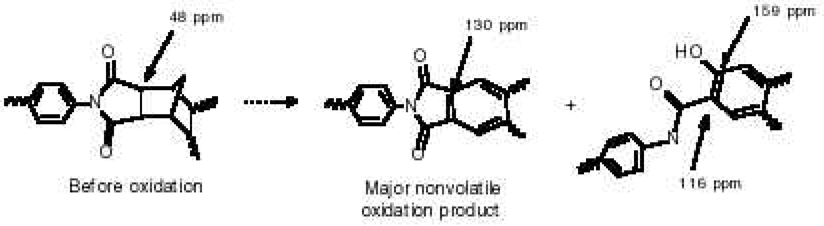
For each step of curing or aging, the solid nuclear magnetic resonance spectrum of natural abundance PMR-15 powder, as well as that of the labeled analog, was determined. Carefully matched experimental conditions allowed the natural abundance spectra to be subtracted from the labeled to obtain difference spectra containing only labeled resonances. In this way, it was possible to follow the transformations of only the labeled carbon. The difference spectrum of the prepolymer consists of a single peak at 46 ppm. On crosslinking, the peak shifts downfield to 48 ppm, indicating that polymerization takes place mainly through path b.

Knowledge of the crosslinking mechanism and the resulting molecular structure is not merely important for understanding how the polymer cures. We can now begin interpreting the degradation reactions occurring in the endcap during long-term aging (ref. 7). The next figure shows difference spectra for endcap-labeled PMR-15 powder aged at 315 °C. After 64 hr, nearly all the peak at 48 ppm is gone. In its place, three broad peaks for labeled carbons grew in at 110 to 120, 125 to 140, and 155 to 165 ppm.



Carbon-13 difference spectra of labeled carbons on nadic endcap shown before and after aging at 315 °C for up to 64 hr.

Though the spectra are complex, these broad peaks suggest (see the following figure) that degradation involves oxidation of the bridging methylene followed by carbon monoxide extrusion to lead to substituted phenyl rings (130 ppm). Further oxidation might lead to breakage of the imide bond and give rise to structures with oxygen directly attached to one of the labeled carbons (159 ppm), with the other labeled carbon at 116 ppm. These results represent the first molecular level evidence of the formation of nonvolatile degradation products from the endcaps, and they give insight into ways to stabilize the endcap for a new generation of crosslinked polyimides.



Possible products of the oxidation of nadic crosslinks shown with chemical shifts predicted from model compounds.

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