

IDENTIFICATION OF LOW-MOLECULAR WEIGHT VOLATIVE THERMAL-OXIDATIVE NYLON 6.6 DEGRADATION PRODUCTS USING SELECTIVE ISOTOPIC LABELING AND CRYO-GC/MS

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INTRODUCTION Polyamides, in particular nylons, are commercially and widely used in automotive parts, carpets, ropes, food packaging, barrier materials, and clothing. Certain high-reliability applications require that nylon fibers are either stored or used for times up to several decades. It is therefore critical to enhance the current knowledgebase of nylon aging, in particular nylon aged under thermal-oxidative conditions as a means to correlate degradation product formation to physical properties. Identification and characterization of degradation species that outgas during nylon aging at specific times can be used as a foundation to create detailed decomposition mechanisms and to develop chemical sensors tailored to monitor specific volatile compounds that can provide early warning of potential changes in the mechanical properties of materials.

METHODS Nylon 6.6 monomers and polymers used in these experiments were: unlabeled adipic acid and 1,6-hexandiamine; C-13 adipic acid; unlabeled nylon; and C-13 and N-15 nylon. Duplicates of all samples were placed in sealed SS vessels (5 cc) and placed within a circulating oven for up to 243 days at 138 °C. Compounds were aged under either ambient conditions or an enriched oxygenated environment (O-18, 99%). Headspace gas was preconcentrated, separated, and detected using cryofocusing gas chromatography mass spectrometry (cryo-GC/MS; Jeol GCMateII). GC chromatograms and mass spectra for all volatile degradation species were compared and used to determine the exact location for isotopically labeled atoms, where applicable.

RESULTS Selective isotopic labeling of monomers, polymers, and aging environments combined with cryo-GC/MS enabled the identification of eighteen volatile low-molecular weight thermal oxidative degradation products of nylon 6.6: butene, butane, carbon dioxide, ammonia, 1-pentene, acetone, methyl acetate, cyclopentene, 2-butanone, tetrahydrofuran, benzene, 2-pentanone, tetrahydropyran, pyridine, toluene, 2-hexanone, cyclopentanone, and water. Highly reproducible gas chromatograms and mass spectra were produced for all unlabeled and isotopically labeled samples. Unlabeled and isotopically labeled (C-13 and N-15) nylon 6.6 monomers and polymer were used to verify the identity of and aid in the understanding of the origin of each degradation product. Nylon 6.6 was also aged under an O-18 enriched environment to better understand the origin of oxygen in degradation products containing one or two oxygen atoms (i.e., an intermolecular oxygen source, an intramolecular oxygen source, or both). The presence of isotopically labeled oxygen atoms was also used to verify the applicable compounds formed *via* thermal-oxidation of nylon 6.6. Relative ratios for unlabeled to isotopically labeled degradation products were used to make general observations regarding compound formation. The exact location of the isotopically labeled ion was determined with absolute certainty for all but three compounds by comparing the mass spectra for the NIST library match, unlabeled nylon, and isotopically labeled species. Knowing the location for isotopically labeled atoms in nylon 6.6 thermal-oxidative degradation products will enable us to map individual compounds onto the nylon 6.6 structure and determine the mechanisms used to form each specific compound. An understanding of the complex degradation mechanisms of nylon 6.6 can be used to develop chemical sensors that detect and monitor for specific molecules that outgas as the polymer ages and thus serve as an indicator for changes in physical properties (ex., a loss in tensile strength or material integrity).

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