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LEVERAGING ISOTOPIC LABELS TO ELUCIDATE THE UNDERLYING DEGRADATION CHEMISTRIES OF NYLON 6.6

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Introduction

To enhance the current knowledge base of polyamide aging, it is critical to understand the chemical degradation mechanisms which contribute to changes in material properties.[1-5] Previous investigations have explored the underlying chemistries associated with nylon 6.6;[6, 7] however, questions still remain regarding mechanistic routes. In the present study, thermal-oxidative accelerated aging studies were performed on neat and isotopically labeled nylon 6.6 at 109 °C and 138 °C for varying time periods. Cryofocusing combined with gas chromatography and mass spectrometry (cryo-GC/MS) was used to identify low molecular weight degradation products of nylon 6.6. The identities of the labeled and unlabeled aging products are being used as the foundation for the iterative process to elucidate underlying degradation mechanisms.

This study demonstrates the details achievable by leveraging isotopically labeled materials in conjunction with cryo-GC/MS analysis. As one example, we provide preliminary results on the origins of carbon dioxide—the most abundant degradation product formed during nylon 6.6 degradation—and discuss the proposed formation mechanisms. Understanding the chemical pathways and volatile products in nylon 6.6 degradation should provide new insights to detect and reduce early aging, better correlate accelerated aging with long-term application environments, and mitigate problems associated with material degradation.

Experimental

Materials. All reagents were used without further purification. Unlabeled nylon 6.6 (99%), ^{13}C labeled nylon 6.6 (99% enriched), and ^{18}O isotopically enriched O_2 ($^{18}O_2$, 99% enriched) were purchased from Isotec Stable Isotope Products (Sigma Aldrich). Figure 1 shows the structures of the nylon 6.6 samples used in this investigation.

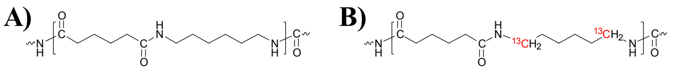

Figure 1. Nylon 6.6 (A) unlabeled and (B) enriched with ^{13}C isotopic labels positioned in the 1,6-hexanediamine fragment.

Instrumentation. Volatile organic compounds (VOCs) in the headspace gas (5 mL) above the aged nylon 6.6 samples were extracted and preconcentrated using cryofocusing (Model 7100A, Entech Instruments, Inc.). The preconcentrated gas packet was transferred through a GC transfer line held at 100 °C before being rapidly injected into the GC (6890N, Agilent Technologies). VOCs in the headspace gas were separated over the course of 52 min using a DB-5MS column (0.25 mm X 60 m, Agilent) with the following GC oven temperature segments: -40 °C hold for 2 min, ramp from -40 °C to 30 °C (9 °C/min), ramp from 30 °C to 150 °C (3 °C/min), and 150 °C hold for 2 min. Mass spectral analysis was performed in conjunction with GC separation using a GCmate II (Jeol USA) mass spectrometer equipped with an electron ionization (EI) source.

Accelerated Aging. Nylon 6.6 was subjected to accelerated aging experiments at temperatures of 109 ± 2 °C or 138 ± 2 °C, for times between 1 and 243 days. Sample masses varied between 10 to 100 mg to ensure the VOCs were present in high enough concentrations to be detected with the mass spectrometer. Specific experiments designed to identify the source of molecular oxygen in key thermal-oxidative degradation products were performed in an ^{18}O isotopically enriched O_2 environment. Gold plated copper gaskets were employed for all accelerated aging experiments to ensure no oxidation products were formed during the accelerated aging process from the metal gaskets at elevated temperatures.

Results and Discussion

Carbon Dioxide. Numerous reports have identified carbon dioxide as a major degradation product of nylon 6.6.[3, 6, 8-11] Figure 2 shows mass spectra identifying carbon dioxide as a thermal-oxidative degradation product of nylon 6.6, which is confirmed by comparing this data to the NIST library spectrum[12] shown in Figure 2B where $CO_2^{+\cdot}$ (*m/z* 44) is the base peak. Figure 2C shows the mass spectrum of CO_2 formed by unlabeled nylon 6.6 in an ^{18}O enriched environment. Mass spectral peaks at *m/z* 44, 46, and 48 are indicative of $CO_2^{+\cdot}$, $CO^{18}O^{+\cdot}$, and $C^{18}O_2^{+\cdot}$, respectively. Identification of mono- and di-isotopically labeled CO_2 with ^{18}O enrichment is critical in discriminating the origin of molecular oxygen in CO_2 and other thermal-oxidative degradation products. All of the experimental spectra shown in Figure 2 were obtained after 1 day of aging at 138 °C.

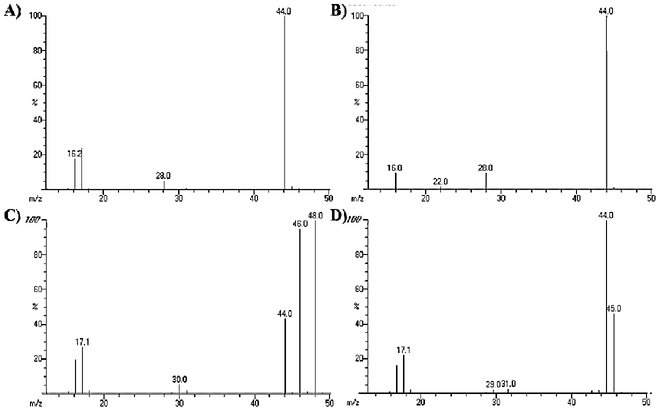

Figure 2. (A) A representative carbon dioxide mass spectrum from oxidation of unlabeled nylon 6.6 and (B) the corresponding NIST Mass Spectral Library match.[12] (C) The carbon dioxide mass spectrum from oxidation of unlabeled nylon 6.6 in an ^{18}O enriched environment. (D) The carbon dioxide mass spectrum from oxidation of ^{13}C labeled nylon 6.6 in an oxygen environment.

Figure 2C shows mass spectral shifts due to ^{18}O enrichment. The presence of mono-isotopically labeled $CO^{18}O$ in these initial results indicates that significant amounts of the total CO_2 present likely originate from the carbonyl carbon of the amide group in nylon. The carbonyl carbons make up 1/6th of the carbons in the nylon 6.6 repeat unit; however, the carbonyl carbons contribute a significant portion of CO_2. The remaining CO_2 generated during degradation comes from the other carbons in the nylon backbone, identified as ^{18}O di-isotopically labeled $C^{18}O_2$. Mass spectra for degradation times of up to 243 days were very similar to the mass spectrum depicted in Figure 2C. Further experiments are underway to verify these results, and to extend the measurements to longer degradation times and lower temperature.

Accelerated aging studies on ^{13}C enriched nylon 6.6 (carried out under an air atmosphere having unlabeled oxygen) also provided insightful results, as shown in Figure 2D. Mass spectral analysis demonstrated that a minority of the CO_2 formed originated from the methylene groups adjacent to the nitrogen atoms, as indicated by the presence of $^{13}CO_2$ (*m/z* 45). A free radical attack on a hydrogen atom located in the methylene group adjacent to the nitrogen followed by oxidation ultimately results in CO_2 formation and chain scission. Further free radical propagation can also lead to ammonia production. ^{13}C labeling thus afforded the opportunity to elucidate the genesis of CO_2 from the *n*-vicinal methylene group. Figures 3 and 4 show a summary of the mechanisms consistent with the experiments performed on nylon 6.6. Similar to prior workers,[11] we expect that the hydrogens most susceptible to initial free radical extraction are in the methylene group adjacent to the nitrogen. This is consistent with mechanistic insight from small-molecule free-radical chemistry, which shows a strong activation of a methylene group adjacent to a nitrogen atom, with regard to radical attack.[13, 14] Carbonyl carbon also activates an adjacent methylene group, although less strongly compared with the effect of nitrogen. Thus, initial radical abstraction as indicated in Figures 3 and 4 may be expected.[13] Note that additional mechanisms will be operating as well; for example, carbon-centered free radicals in these mechanisms are shown as reacting with O_2, but they can also react by other mechanisms, such as abstraction of a hydrogen atom from an adjacent chain, leading to products other than CO_2. Additionally, the C-N bond cleavage, shown in line 2 of Figure 3, results in a free radical on nitrogen which could continue oxidative reactions leading to eventual expulsion of CO_2 from what had been the amide carboxyl group. Note that in Figures 3 and 4, to save space, we are showing the outcomes of both ^{13}C labeling and also ^{18}O labeling in terms of the CO_2 product generated. However, the ^{13}C and ^{18}O labeling were actually two separate experiments.

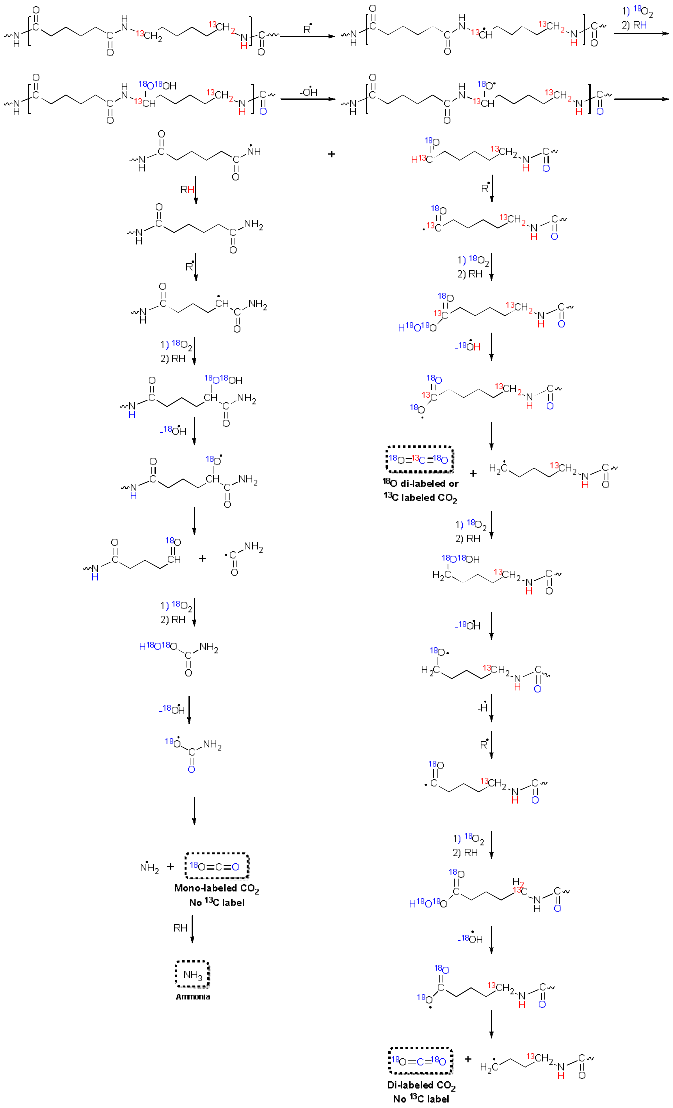

Figure 3. Proposed thermal-oxidative degradation mechanisms of nylon 6.6, which show the varying origins of carbon dioxide.

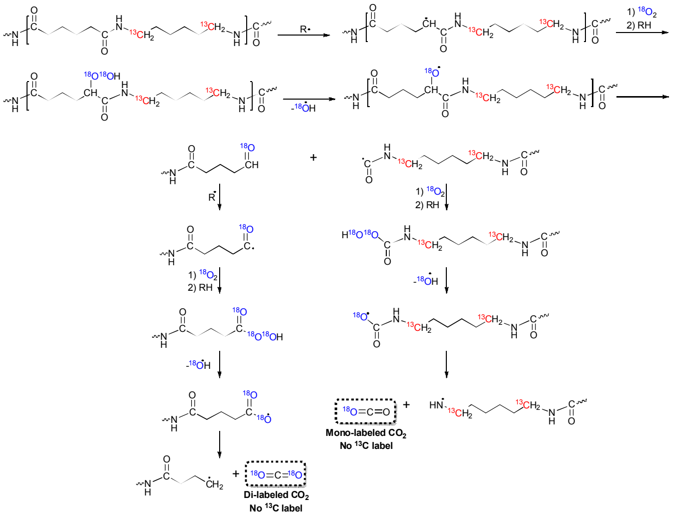

Figure 4. Proposed thermal-oxidative degradation mechanisms of nylon 6.6, which show the varying origins of carbon dioxide.

Benzene, Pyridine, and Cyclopentanone. Figure 5 shows some of the other nylon 6.6 degradation products that have been identified. Future work will discuss the mechanisms leading to these molecules.

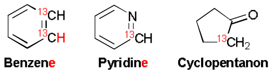

Figure 5. Some thermal-oxidative degradation species identified by mass spectral analysis, including the location of ^{13}C isotopic labels.

Conclusions

By leveraging isotopic labels in conjunction with cryo-GC/MS analysis, we are studying the origins of CO_2—the most abundant thermal-oxidative degradation product of nylon 6.6. Ongoing efforts include elucidation of the degradation mechanisms for other key thermal-oxidative degradation products. This work investigates a new methodology expected to provide insights for material degradation and applies this method to gaining information on the thermal-oxidative degradation of nylon 6.6.

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