NMR Analysis of UV- and Heat-Aged Nylon-6,6

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ABSTRACT: Samples of Nylon-6,6 were analyzed by 1-D and 2-D NMR techniques to determine the degradation structures resulting from UV exposure of Nylon films and heat aging of Nylon pellets. The dominant degradation structure in all cases was the terminal methyl group which was attributed to chain scission reactions. Further evidence for chain scission was found through the presence of aldehyde and formamide structures upon UV exposure and heat aging (in the presence of air) and terminal vinyl structures upon UV exposure. The presence of oxygen during UV exposure resulted in OH substitution adjacent to the amide group and at the end of a cleaved alkyl chain. Terminal amide groups were observed in the starting material and did not increase in concentration upon heat aging or UV exposure. In heat-aged samples, no evidence was found for olefinic or hydroxyl-containing structures in nitrogen, but hydroxyl structures were observed. A degradation mechanism was proposed to account for the structures observed in our work.

Introduction

Nylon materials in general, and Nylon-6,6 in particular, are useful polymers due to their excellent chemical resistance and thermal stability with relatively high temperatures.[1,2] Thus, the Nylon-6,6 polymer is used in a wide variety of applications such as monofilament, electrical, and electronic connectors and underhood automotive parts. Additionally, due to excellent wear resistance, Nylon-6,6 is widely used in fiber applications including carpets and tire yarns. Nearly all applications for Nylon-6,6 are subject to either high heat or large amounts of incident UV light (in the form of sunlight or interior lighting). Thus, there is a fundamental science interest in understanding the degradation chemistry of UV exposure and heat aging of Nylon-6,6.

The goals of this work were to assign the chemical microstructural changes caused by degradation, to compare and contrast these results in heat-aged and UV-exposed systems, and to use this information on these structures to understand the underlying degradation chemistry.

A literature review of the NMR spectroscopy of nylon materials indicates that the vast majority of the NMR work has been dedicated to determination of bulk chemical composition or study of motional changes in the solid state. Only two papers have dealt with determination of the smaller microstructural details in Nylon-6,6.[3,4] The first paper, by de Vries, Linssen, and Velden,[3] used a variety of 1-D and 2-D NMR techniques, coupled with model compound work, to assign the various chain end structures for Nylon-4,6, Nylon-6,6, and Nylon-6. The other work, by Steadman and Mattias,[4] assigned the chain ends, the *cis*/*trans* amide conformer and cyclic monomer peaks in the ^{13}C spectrum for Nylon-6,6 and Nylon 6.

Several different NMR experiments were used in this present study to elucidate the chemical microstructural changes in these samples. ^{1}H direct detection experiments were used to identify all unique proton structures present. DEPT (distortionless enhancement by polarization transfer[5]) experiments were used in conjunction with the ^{13}C direct experiment on the 10 day exposed UV degraded material to identify the number of directly bonded protons to each carbon. In the DEPT experiment used in this work (DEPT-135), carbons with an odd number of directly bonded protons appear as positive peaks, even number of directly bonded protons appear as negative peaks, and nonprotonated carbons are absent or present at a few percent of the original intensity. Thus, this experiment allows the determination of the number of directly bonded protons. ^{13}C direct detection was performed on the sample which exhibited the greatest number of degradation structures as a preliminary means of determining the amount of additional information that could be obtained by this experiment. ^{15}N direct detection was investigated, but the low sensitivity of natural abundance ^{15}N in Nylon-6,6 eliminated this as a useful technique for this study.

Several 2-D NMR experiments were also used in this work. The primary 2-D NMR experiments used were HMQC (heteronuclear multiple quantum coherence) experiments. HMQC[6−8] is an indirect detection experiment; that is, X-nucleus magnetization is detected via proton signals. The resulting 2-D spectrum contains the X-nucleus chemical shift information on one axis (such as ^{13}C or ^{15}N) and the proton chemical shift information on the other axis. This has the major advantages of providing two different chemical shifts to a given unknown resonance and for separating out the overlap in one chemical shift range by the use of a second chemical shift range. This is especially important in ^{1}H NMR spectroscopy due to the limited chemical shift range; the 2-D experiments allow separation of the proton peaks via the ^{13}C (or ^{15}N) chemical shift. Combining the 2-D and 1-D NMR work allowed many possible assignments to be studied using multiple peak

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shifts; this allowed many resonance assignments to be definitively made.

The UV exposure experiments were performed on blown films of Nylon-6,6. The advantage of this approach was that the whole sample was degraded, not merely the surface; thus, isolation of a degraded surface layer from a nondegraded bulk was not required. The heat aging was performed on Nylon-6,6 pellets used as is. Degradation under air was chosen in order to apply the knowledge gained to actual use applications.

Experimental Section

All NMR work was performed on Varian Unity 500 systems. The ^{1}H direct and all HMQC experiments were performed using a Nalorac 3 mm indirect detection probe, while the ^{13}C direct, ^{15}N direct detection, and DEPT experiments were performed using a standard Varian 5 mm multinuclear probe. Direct detection experiments were performed spinning at 20 Hz, while all HMQC experiments were performed nonspinning. No proton decoupling was used for any of the HMQC experiments. All measurements were taken at 30 °C. Proton experiments were collected with 512 scans, a ^{1}H spectral frequency of 499.8 MHz, a ^{1}H spectral width of 6441 Hz (13 ppm), and a recycle delay of 1 s. ^{13}C HMQC experiments were performed using 256 steps, a J(CH) of 140 Hz, a ^{13}C spectral frequency of 125.697 MHz, 56−90 repetitions, a ^{1}H spectral width of 4662 Hz (9.3 ppm), a ^{13}C spectral width of 8000 Hz (64 ppm), and a recycle delay of 1 s. One ^{13}C HMQC experiment was performed using a wider sweep width (31 250 Hz, 248 ppm) and a J(CH) of 190 Hz to detect aldehyde and olefinic structures. The ^{15}N HMQC experiment used a J(NH) of 90 Hz, a ^{15}N spectral frequency of 50.6 MHz, a ^{15}N spectral width of 2500 Hz (49 ppm), and 128 increments with 144 repetitions. ^{13}C and DEPT direct detection experiments were performed using 40 000 scans for the ^{13}C direct detection experiment, 10 000 scans for the DEPT experiment, and a recycle delay of 1 s for both types of experiments. ^{15}N referencing was performed by setting the main amide nitrogen peak to 253.9 ppm.[9] Proton NMR referencing set the HFIP CH peak to 4.4 ppm,[10] while the ^{13}C referencing was performed by setting the amide carbonyl peak to 175.72 ppm.[4]

Samples for NMR were prepared by taking the material and dissolving it in a 3 or 5 mm NMR tube using hexafluoro-2-propanol-d_2 (HFIP-d_2) obtained from Isotec Inc. (Miamisburg, Ohio). For all NMR work, the concentrations were approximately 0.2 mg/μL of HFIP-d_2 solvent. Care was taken in handling HFIP-d_2, as it is capable of producing serious chemical burns. A fuller description of the hazards of HFIP-d_2 is available from the Material Safety Data Sheet.

Heat-aged samples were prepared by placing 100 g of commercial grade Nylon-6,6 (Monsanto Vydyne 21) in a preheated oven at 125, 150, or 175 °C for 72 h in an air atmosphere. The samples were then cooled in air and placed in a sealed foil bag. The sample, heat aged at 90 °C, was prepared by taking Nylon-6,6 pellets and exposing them in an air oven on a watch glass for 17 days at 90 °C. The sample, heated at 175 °C for 3 days, was insoluble and was not used for this study.

UV degradation samples were prepared by taking 3 mil thick blown films of Nylon-6,6 and exposing them for 5 and 10 days in a UVCon Weatherometer using a UVB-313 set at 70 °C for the UV cycle and at 50 °C for the condensate cycle. The weathering cycle was 30 min water preheat, 8 h UV exposure, and 4 h condensate exposure. The last two steps were then repeated for up to 5 or 10 days as needed. The Nylon-6,6 material used for UV exposure was a commercial grade solid-state polymerized Nylon-6,6 available from Monsanto (Vydyne 66B). The 3 mil thick films were prepared by film blowing using the experimental conditions listed in Table 1.

Quantitation of the ^{1}H spectra was performed using the assumption that the degree of saturation was constant for all peaks. In a spin system such as ^{1}H in which strong spin diffusion and only one phase exist, this is a good assumption; however, should the material phase separate the assumption is invalid.

Table 1. Film Blowing Conditions

region	set point temp (°C)	actual temp (°C)/other data
zone 1	250	248
zone 2	266	305
zone 3	285	285
zone 4	285	284
zone 5	285	294
zone 6	285	286
zone 7	285	288
extrusion RPM		22
extrusion PSI		1650
nip roll speed		7.4
fan speed		2.6

Molecular weight determination was performed using a modular liquid chromatograph consisting of a Waters Model 590 pump, Model 712 WISP autosampler, Model KMX-6 low-angle laser light scattering photometer, and a Viscotek Model 200 combined refractive index detector and differential viscometer. The columns used were two PSS gel 10 μm linear SDV columns, PSS-USA (Polymer Standards Service) Houston, Texas. The solvent used was hexafluoro-2-propanol with 0.08% sodium trifluoro acetate added. The samples were chromatographed at a flow rate of 0.5 mL/min with an injection volume of 50 μL. The column temperature was maintained at 46 °C, and sample concentrations were approximately 2.5 mg/mL. Data acquisition and processing were performed using Trisec software written by Viscotek Corp., Houston, Texas.

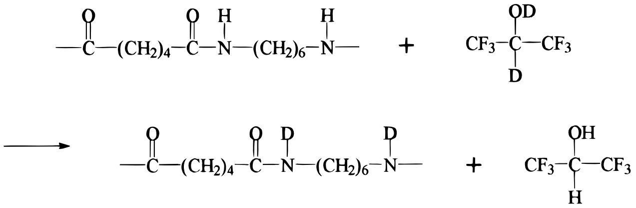
Results and Discussion

Despite the large interest in Nylon degradation, there is a scarcity of NMR information in the literature dealing with the microstructure of nylons, other than the assignment of the main chain resonances. The two works that do exist in this area have assigned carboxylic and amine chain ends[3,4] and the *cis* conformers;[4] there has been no NMR work to follow degradation structures and chemistry. NMR allows the degradation structures to be directly determined; additionally, the advent of high-field NMR systems has dramatically increased the sensitivity of the technique. There is a limitation to this approach; the material must still be soluble. While it is possible to perform solid-state NMR experiments, the sensitivity and resolution are drastically reduced and the type and amount of information available from solution spectra can be lost.

The basic organization of this paper will be to discuss the ^{1}H spectrum of the control material first. This serves to identify any smaller microstructural features which exist initially. The next two sections will then analyze the UV exposure results and the effect of heat aging.

Nylon-6,6 Control

Figures 1−4 illustrate the proton spectrum of the Nylon-6,6 control sample. Figure 1 is an overview of the full spectral window. The peak at 6.3 ppm is the amide proton; this peak is weak due to exchange between the amide protons and the −OH peak of the solvent (HFIP-d_2, hexafluoro-2-propanol-d_2):



$$-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}- \;+\; CF_3-\underset{D}{\overset{OD}{C}}-CF_3$$

$$\longrightarrow -\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{D}{\overset{|}{N}}-(CH_2)_6-\overset{D}{\overset{|}{N}}- \;+\; CF_3-\underset{H}{\overset{OH}{C}}-CF_3$$

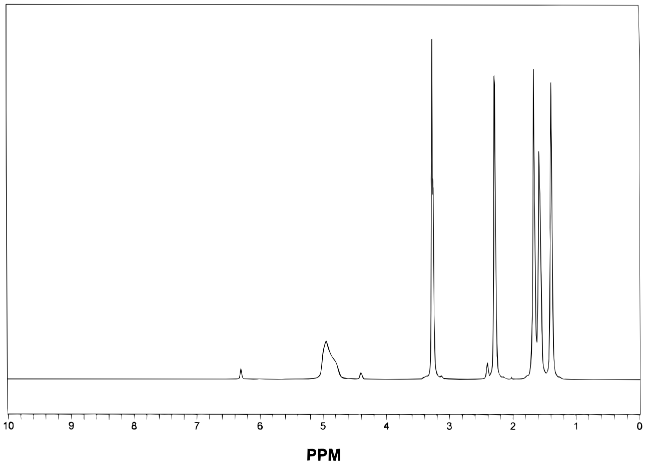


Figure 1. ^{1}H NMR spectrum of Nylon-6,6 control.

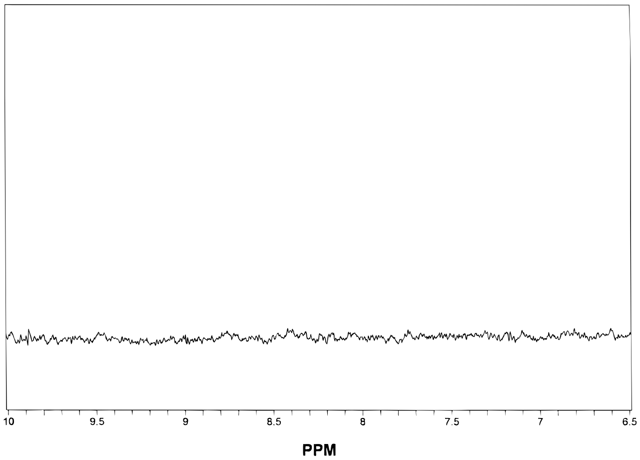


Figure 2. ^{1}H NMR spectrum of Nylon-6,6 control illustrating an enlargement of the region from 10.0 to 6.5 ppm.

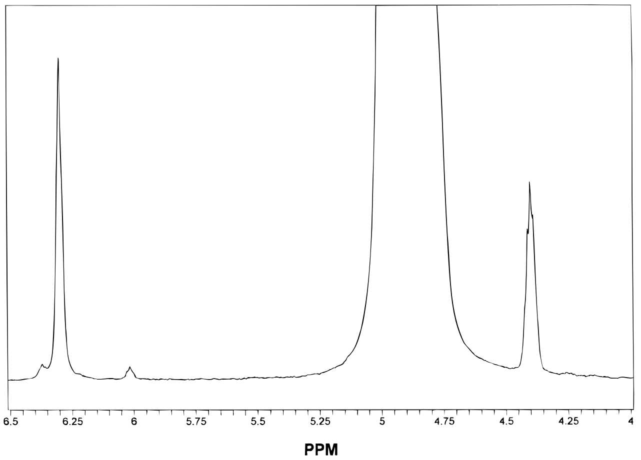


Figure 3. ^{1}H NMR spectrum of Nylon-6,6 control illustrating an enlargement of the region from 6.5 to 4.0 ppm.

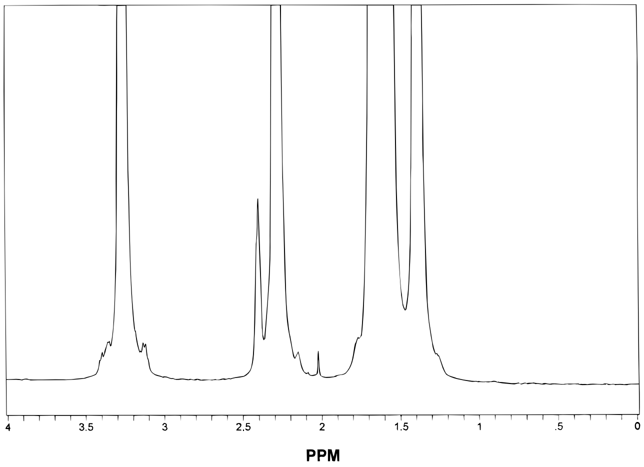


Figure 4. ^{1}H NMR spectrum of Nylon-6,6 control illustrating an enlargement of the region from 4.0 to 0.0 ppm.

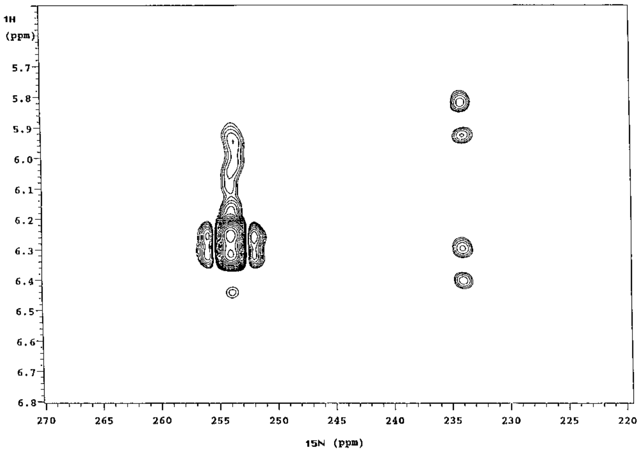
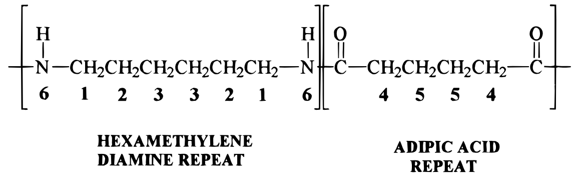


Figure 5. ^{15}N HMQC spectrum of Nylon-6,6 control.

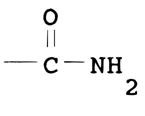
The HFIP −OH peak is the small peak at 4.4 ppm, while the broad resonance at approximately 4.9 ppm is due to absorbed water. The remaining protons can be assigned using the following numbering scheme:



$$\left[-\overset{H}{N}-CH_2CH_2CH_2CH_2CH_2CH_2-\overset{H}{N}-\right]\left[-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-\right]$$

The peak at 3.3 ppm is the methylene **1**, while the peak at 2.2 ppm is methylene **4**. The remaining protons were assigned via literature work;[3,4] protons **5** appear at 1.7 ppm, while the resonances 1.6 and 1.2 ppm can be assigned to methylene protons **3** and **2**, respectively.

Enlargement of the base line region of this spectrum yields several smaller peaks. Figure 2 illustrates the region of the proton spectrum between 10 and 6.5 ppm for the Nylon-6,6 control sample. There are no peaks in evidence in this region; the significance of this will be apparent later. Figure 3 contains the region from 6.5 to 4.0 ppm. The peak at 6.3 is due to the amide group (as discussed previously). Figure 5 helps to elucidate the structure which gives rise to the peaks at 6.4 and 6.0 ppm. Figure 5 is the ^{15}N HMQC experiment for the 10 day UV exposure sample; the peaks at 6.4 and 6.0 ppm appear in both the control and degraded samples. The peaks at 6.4 and 6.0 ppm have identical ^{15}N chemical shifts; additionally, this region of the ^{15}N spectrum is characteristic of amide nitrogens.[9] Thus, these peaks result from a primary amide structure:



$$-\overset{O}{\overset{\|}{C}}-NH_2$$

The splitting is due to the limited rotation around the C−N bond in an amide group; the delocalization of the electrons through this bond results in slow rotation

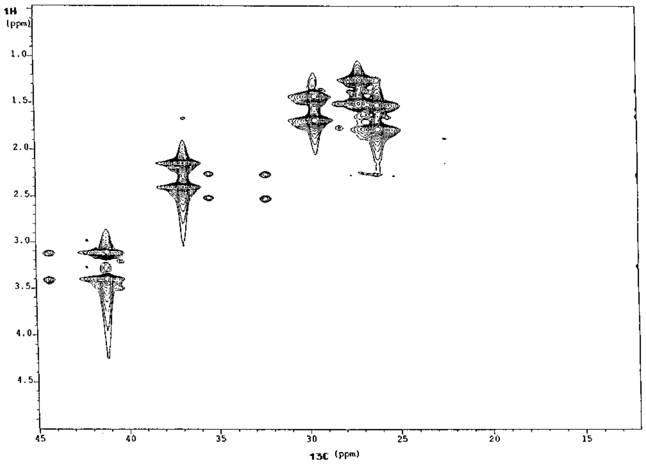
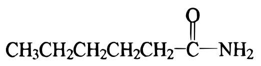


Figure 6. ^{13}C HMQC spectrum of Nylon-6,6 control.

relative to the NMR time scale. Supporting evidence for this arises from the reference spectra of alkyl primary amides, which all show unique chemical shifts for both amide protons.[10] Additionally, hexanamide, which is a very close model for this proposed structure, exhibits amide proton peaks at 6.4 and 6.0 ppm. The



$CH_3CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-NH_2$

Hexanoamide

strength of the water peak at 4.8 ppm arises primarily from absorbed water in the Nylon-6,6 (Nylon-6,6 is an excellent absorber of ambient moisture).

Figure 4 contains the aliphatic region for the control sample. There are several small peaks near the base of these peaks; they include peaks due to methylene groups near the carboxylic and amine chain ends, methylenes near the cis amide conformer, and resonances due to a cyclic monomer. It should be noted that in the control sample there are no peaks upfield of 1.2 ppm. This is not the case for the degraded materials, as will be shown later.

Figure 6 illustrates the ^{13}C HMQC spectrum for the control sample. The HMQC experiment exhibits the five main resonances and several smaller resonances. The large peak at 41.4/3.3 ppm (^{13}C/^{1}H chemical shifts) is methylene **1**, while the large peak at 36.8/2.3 ppm is methylene **4**. The peak at 29.4/1.5 ppm is methylene **3**, while methylene **2** and methylene **5** appear at 22.0/1.9 ppm. There are also smaller peaks at 44.5/3.3, 42.1/3.2, 40.3/3.4, 35.5/2.4, and 32.2/2.4 ppm. According to the work of Steadman and Mathias,[4] the peaks at 44.5/3.3 and 32.2/2.4 are due to the cis conformer. There should also be two additional peaks in the HMQC spectrum for this structure, but due to the reduced resolution of the 2-D experiment in the F1 (^{13}C) direction, these peaks are not observed, as they are buried in the large resonances at 30 and 25 ppm. Also according to the work of Matthais and Steadman, the peak at 42.1/3.2 is a methylene group adjacent to a chain end amine, while the peak at 35.5/2.4 ppm is a methylene adjacent to a chain end carboxylic acid. The small peak at 40.3/3.4 ppm is the methylene group adjacent to the amide NH in the cyclic monomer. The methylene group adjacent to the carbonyl in the cyclic monomer is not observed, but is very likely lost in the F1 (^{13}C) "tail" of the peak at 36.8/2.3 ppm.

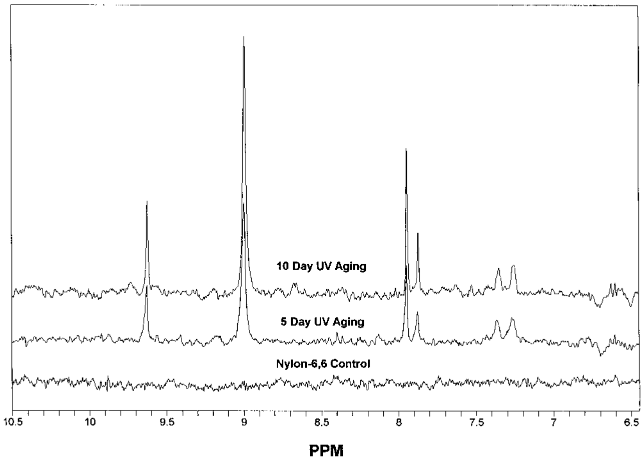


Figure 7. ^{1}H NMR comparing the region from 10.0 to 6.5 ppm for the Nylon-6,6 control and 5 day and 10 day UV aged samples.

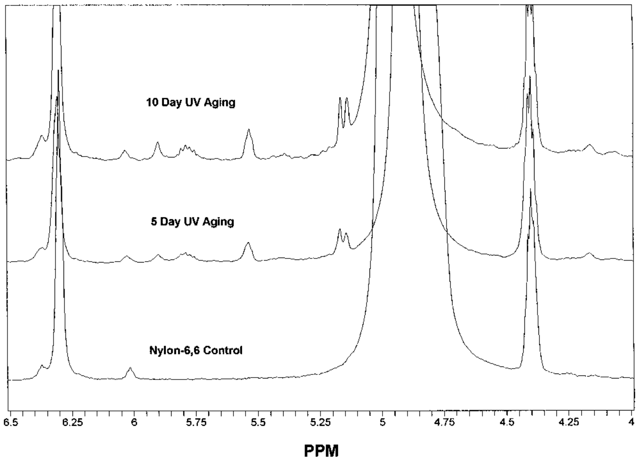


Figure 8. ^{1}H NMR comparing the region from 6.5 to 4.0 ppm for the Nylon-6,6 control and 5 day and 10 day UV aged samples.

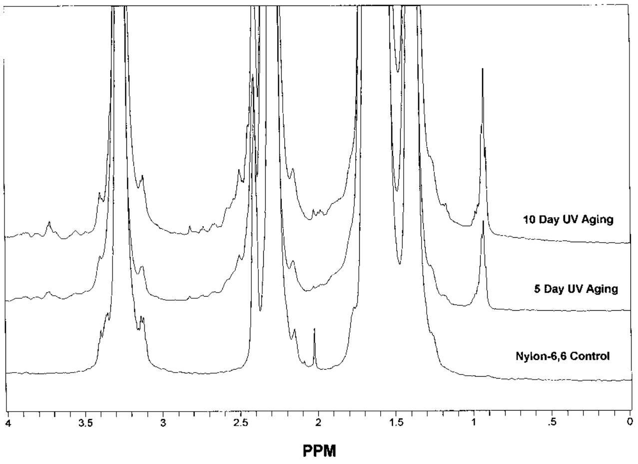


Figure 9. ^{1}H NMR comparing the region from 4.0 to 0.00 ppm for the Nylon-6,6 control and 5 day and 10 day UV aged samples.

UV Degradation of Nylon-6,6 Films

Figures 7−9 show various regions of the proton spectrum of the Nylon-6,6 control material, 5 day UV-exposed material, and 10 day UV-exposed material compared directly. Figure 7 is the spectral region from 10 to 6.5 ppm for this sample. There are several new peaks at 9.6, 9.0, 8.0, 7.9, 7.4, and 7.2 ppm. The source of these new peaks becomes evident by using the ^{13}C

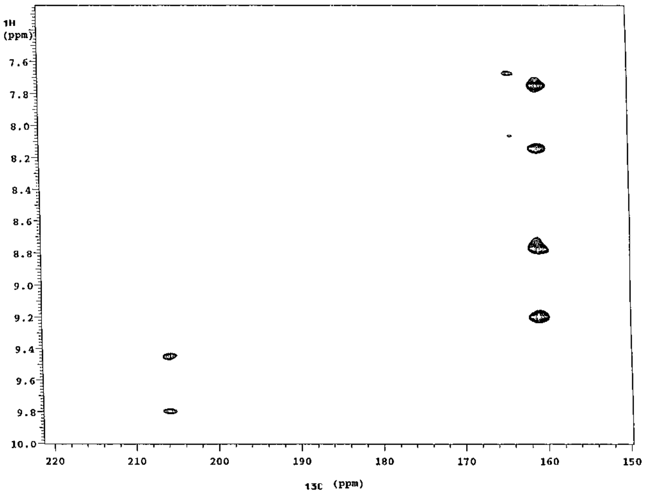


Figure 10. ^{13}C HMQC spectrum (J(CH) = 190 Hz) of 10 day UV aged sample illustrating the aldehyde and formamide peaks.

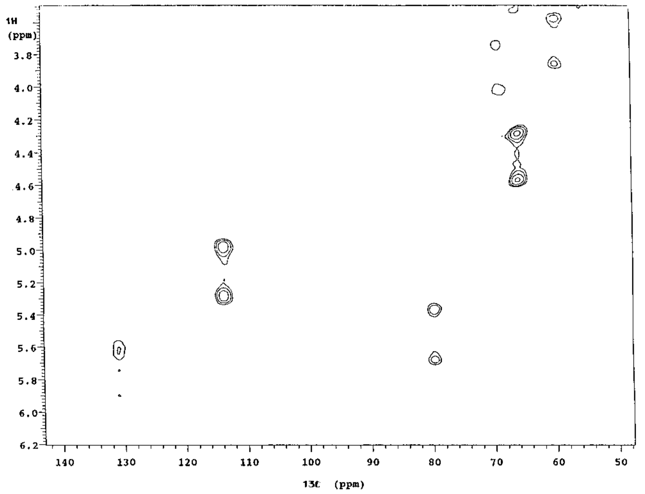
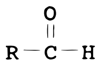


Figure 11. ^{13}C HMQC spectrum (J(CH) = 190 Hz) of 10 day UV aged sample illustrating the various olefinic- and hydroxyl-related peaks.

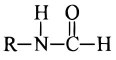
HMQC spectrum shown in Figure 10. The peak at 9.6 ppm corresponds to a ^{13}C chemical shift of 206 ppm; this is consistent with an *n*-alkyl aldehyde structure:



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}H}$$

Where R is a n-alkyl chain

Similar compounds such as octyl and nonyl aldehydes have ^{13}C shifts of 203 ppm and H-1 chemical shifts at 9.75 ppm.[10] Also in Figure 10 are two peaks at 8.0 and 9.0 ppm (^{1}H chemical shifts) which have identical ^{13}C chemical shifts of 161 ppm. On the model compound work,[10] we have assigned these peaks to *N*-formamide structures:

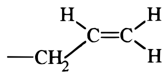


$$\mathrm{R{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}H}$$

The splitting of the formamide structure is probably due to slow rotation of the N−C bond on the NMR time scale. The small peak at 7.9 ppm is a slight difference in chemical structure of the formamide; the exact structure is not known at this time but may be related to substitution on the carbon adjacent to the formamide linkage. It should also be noted that these peaks were observed in HMQC experiments in which a J(CH) value of 190 Hz was used and were not observed in experiments using a J(CH) value of 140 Hz; 190 Hz is a typical J(CH) value for aldehyde and formamide systems,[11] while 140 Hz is typical of alkyl carbons.

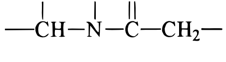
There are also two small peaks at 7.4 and 7.2 ppm in this region. These chemical shifts are nearly identical to the amide proton in ϵ-caprolactam, which has an observed proton shift of 7.3 ppm. Since we were unable to obtain the pure Nylon-6,6 cyclic monomer, ϵ-caprolactam was used as a reasonably close model compound. As mentioned before, there is also a small peak in the control sample which was assigned to the cyclic monomer; this provides further supporting evidence. While these peaks were not observed in the control sample, due to the fact that there is exchange between the solvent and amide groups, the peak may not be observed at lower concentrations.

Figure 8 shows the region of the UV-degraded film from 6.5 to 4.0 ppm. In addition to the amide peaks at 6.4, 6.3, and 6.0 ppm discussed previously for the control sample, there are several new peaks at 5.9, 5.8, 5.5, and 5.1 ppm. The source of these peaks becomes evident in Figure 11, which is the ^{13}C HMQC experiment with a J(CH) of 190 Hz. The peak at 5.9 ppm has a ^{13}C chemical shift of 131 ppm, while the peak at 5.1 ppm has a ^{13}C chemical shift of 114 ppm. Additionally, the DEPT experiment indicated that the peak at 131 ppm is a CH carbon and 114 ppm is a CH_2 carbon. Again, according to this data and model compound work,[10] these peaks are due to a terminal olefinic structure:

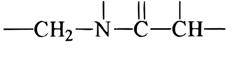


Compounds such as 1-pentene and 1-hexene have ^{13}C chemical shifts of 139 and 114 ppm and ^{1}H shifts of 5.8 and 5.0 ppm for the olefinic carbons and protons. The =CH carbon peak is shifted somewhat upfield; this is the expected affect for an amide group γ to a double bond. This suggests that the olefinic group is forming on an adipic acid residue, but this is not proven at this point. The peaks at 80 and 69 ppm (Figure 11) are CH peaks while 60 ppm is a CH_2 peak based on the DEPT spectrum. The peak at 66/4.4 ppm is the CH carbon in HFIP-d_2. It is important to note that the peaks at 60 and 69 ppm are either not observed or observed only very weakly in the proton spectra; thus, these are very minor structures in the degraded material. The peak at 60 ppm is consistent with a terminal alcohol, while 80 and 69 ppm are consistent with hydroxy substitution adjacent to the nitrogen and the carbonyl side of the amide linkage, respectively:

$-CH_2-OH$



$$\mathrm{{-}\overset{OH}{\overset{|}{C}}H{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}}$$



$$\mathrm{{-}CH_2{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{OH}{\overset{|}{C}}H{-}}$$

Figure 9 shows the proton spectrum in the far upfield region for this sample. Note the strong methyl group peaks at 0.9 ppm; the coupling to an adjacent methylene group is evident.

Figure 12 shows the ^{13}C HMQC spectrum using a J(CH) of 140 Hz, which is a typical aliphatic carbon−proton coupling. Several of the small resonances were assigned previously; these include the cis peaks at 44.5/3.3 and 32.2/2.4 ppm, the cyclic monomer at 40.3/3.4, and the carboxylic acid chain end resonance at 35.5/2.4 ppm.[3,4] The peak at 42.1/3.2 ppm due to amine chain

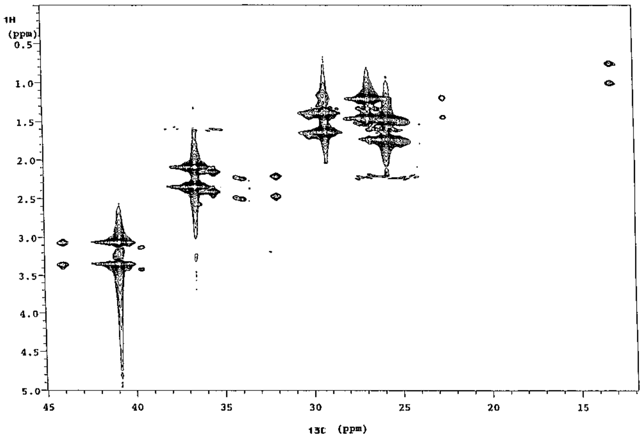


Figure 12. ^{13}C HMQC spectrum (J(CH) = 140 Hz) of 10 day UV aged sample illustrating the aliphatic region.

Table 2. End Group Analysis

sample	COOH (meq/kg)	NH_2 (meq/kg)	relative viscosity
pellet control	94.4	37.6	52
3 days at 125 °C	82	28	44
3 days at 150 °C	0	16	59
blown film control	36	29.3	92.5, 94.6
10 day UV exposure	119	13.6	9.1, 10.9

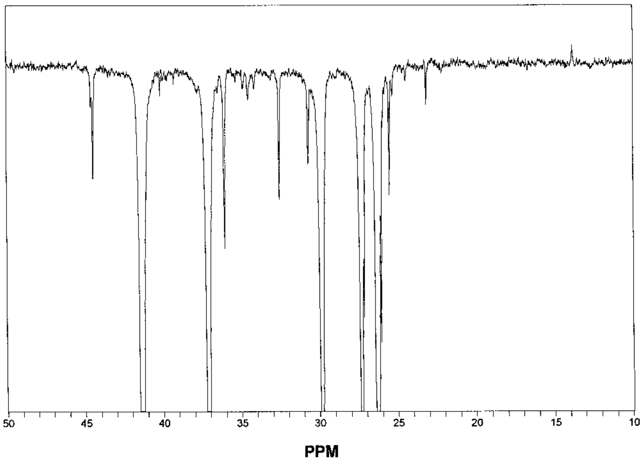


Figure 13. DEPT-135 spectrum of the 10 day UV aged sample illustrating the same region as shown in the 2-D ^{13}C HMQC spectrum in Figure 12.

ends is not observed; this is consistent with the end group analysis data in Table 2, in which the amount of the amine end group is severely diminished upon UV exposure. Thus, the peak is still present, but below the level of detection under these experimental conditions.

There are also several new peaks observed in the spectra in Figure 12 at 34.5/2.4 (two highly overlapped peaks), 23.0/1.3, and 13.7/0.9 ppm. The DEPT spectra in Figure 13 indicate that the only non-methylene carbon in the region from 43 to 0 ppm is the peak at 13.7/0.9 ppm. Thus, the peaks at 23.0/1.3 and 13.7/0.9 ppm are assigned to a terminal $-CH_2CH_3$ structure, which is consistent with an n-alkyl type end group.[10] The two highly overlapped peaks at 34.5/2.4 ppm are most likely due to methylene carbons adjacent to the formamide structures.

Figure 14 shows the carbonyl region of the 10 day UV-exposed sample. The assignment of this region is helped by the work of Steadman and Matthais.[4] The large resonance at 175.7 ppm is the *trans* amide carbonyl, while the *cis* amide carbonyl appears at 176.6 ppm. The carboxylic acid chain end is the resonance at 179.2 ppm, while the cyclic monomer carbonyl is the small resonance at 178.0 ppm. The peak at 163 ppm arises from the formamide structures discussed previously. This region provides significant confirmation for the assignment of the small resonances in the HMQC spectra (Figures 6 and 12).

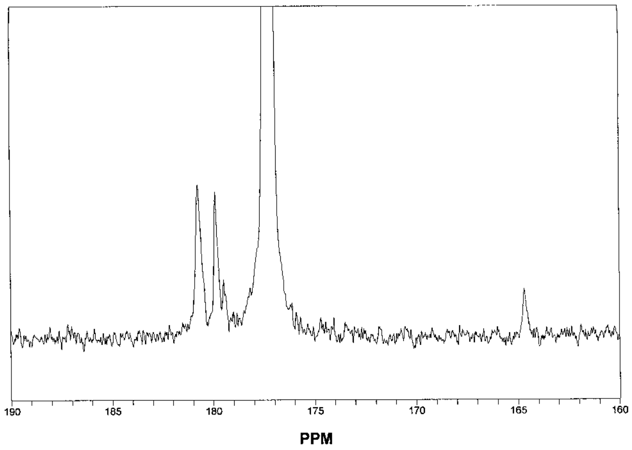


Figure 14. ^{13}C NMR spectrum of the carbonyl region of the 10 day UV aged sample.

Table 3. Molecular Weight Measurements

sample	M_z (1000)	M_w (1000)	M_n (1000)	M_w/M_n
blown film control	84.0	53.5	20.8	2.58
5 day UV exposure	103.0	21.6	4.40	6.64
10 day UV exposure	335.0	34.7	5.63	6.22
Nylon-6,6 pellet control	52.4	36.4	19.6	1.86
17days at 90 °C	44.3	30.6	15.2	2.01
3 days at 125 °C	55.4	35.5	15.8	2.28
3 days at 150 °C	68.6	41.5	13.0	3.20

Molecular weight determination was also performed on the unexposed Nylon-6,6 film and the film after 5 and 10 days of UV exposure. The results are shown in Table 3. The molecular weight is diminishing rapidly with UV exposure up to 5 days, but shows a small increase from 5 to 10 days. Due to the large drop in both number average (M_n) and weight average (M_w), the largest reactions occurring are chain scission reactions. This is consistent with the large amount of formamides, aldehydes, olefinic, and methyl groups arising from chain scission reactions. The increase in the M_z value indicates that there is a small amount of cross-linking also occurring.

Heat Aging (Air) of Nylon-6,6 Pellets

Figures 15−17 show the proton spectrum of the heat-aged samples compared to the Nylon-6,6 control and the 10 day UV-exposed sample. Figure 15 is the region of the ^{1}H NMR spectrum containing the aldehyde, formamide, and cyclic monomer peaks discussed previously. The samples aged at 125 and 150 °C exhibit small amounts of aldehyde and formamide structures and no evidence for the cyclic monomer. The 17 day/90 °C sample contains significant amounts of aldehyde and formamide and also contains several new peaks at 8.4 and 8.2 ppm. These peaks are as yet unassigned, but on the basis of the general category of peaks in this region coupled with the known peaks, several possible assignments can be discussed. These peaks must arise from some form of aldehyde/formamide type structure. Possible structures include a disubstituted formamidenitrogen and formation of an alcohol

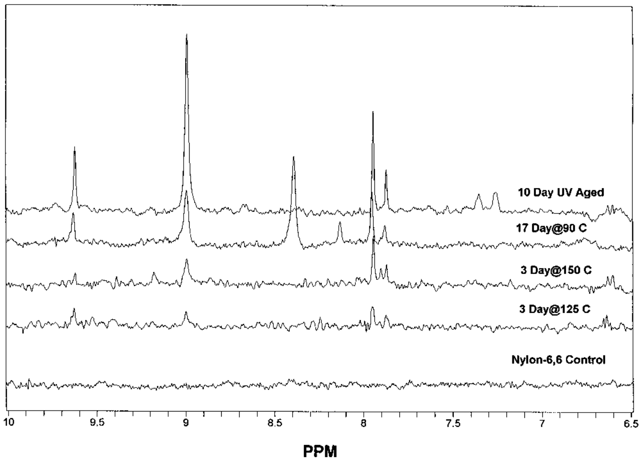


Figure 15. ^{1}H NMR comparing the region from 10.0 to 6.5 ppm for the Nylon-6,6 control and 10 day UV aged and various heat-aged samples.

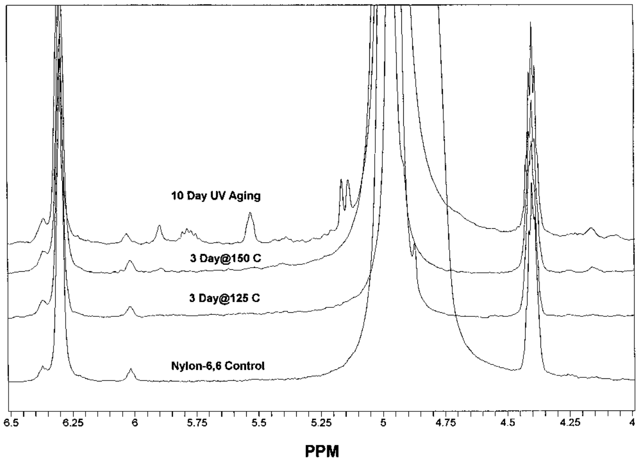


Figure 16. ^{1}H NMR comparing the region from 6.5 to 4.0 ppm for the Nylon-6,6 control and 10 day UV aged, 3 days at 125 °C, and 3 days at 150 °C samples.

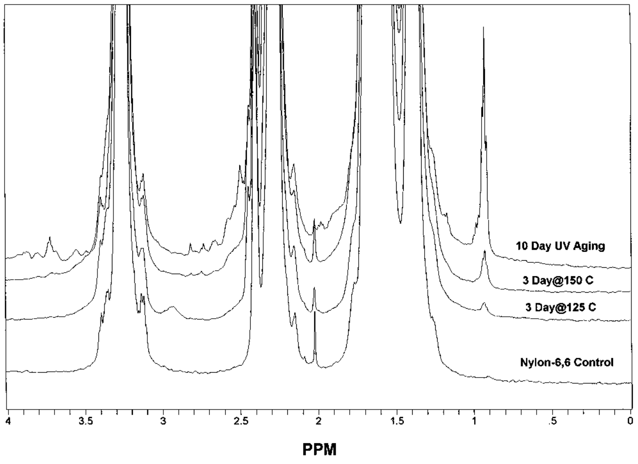
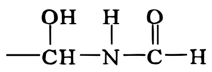
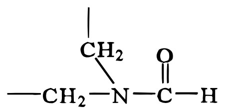


Figure 17. ^{1}H NMR comparing the region from 4.0 to 0.0 ppm for the Nylon-6,6 control and 10 day UV aged, 3 days at 125 °C and 3 days at 150 °C samples.

adjacent to the formamide:



$$-\overset{OH}{\overset{|}{CH}}-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-H$$



$$-CH_2-\overset{\overset{|}{CH_2}}{\overset{\backslash}{N}}-\overset{O}{\overset{\|}{C}}-H$$

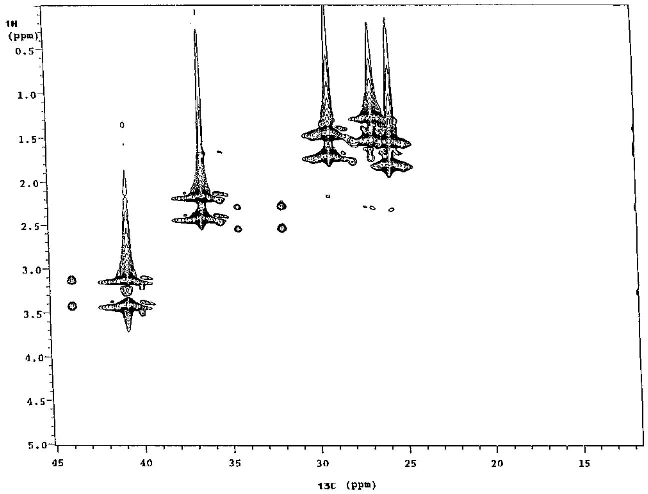


Figure 18. ^{13}C HMQC spectrum (J(CH) = 140 Hz) of 3 days at 150 °C heat-aged sample illustrating the aliphatic region.

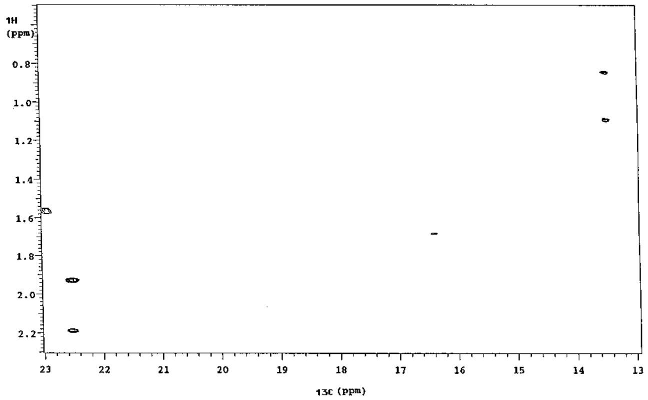


Figure 19. ^{13}C HMQC spectrum (J(CH) = 140 Hz) of 3 days at 150 °C heat-aged sample illustrating an enlargement of the upfield region of Figure 18.

Figure 16 shows the region from 6.5 to 4.0 ppm. Due to complications in this region, the 17 day/90 °C is not of value. The position of the water peak shifts as a function of solution concentration; in this case the region of interest is buried beneath the water peak. In this region there is no evidence for any of the hydroxyl or olefinic structures in the heat-aged material which was found in the UV-exposed material.

Figure 17 shows the region of the proton spectrum from 4.0 to 0.0 ppm. Once again we see that all samples contain the methyl group peak, but the 10 day UV-exposed material has the largest methyl content. Figure 18 shows the ^{13}C HMQC spectrum for the sample aged for 3 days at 150 °C. We can see the peaks due to the *trans* isomer and due to the *cis* isomers and the carbonyl acid chain ends, but there is no evidence for amine ends or the other new peaks which were observed in the UV-exposed sample. Enlargement of the scale does show two weak doublets in Figure 19. This illustrates that the methylene and methyl peaks are indeed present, but are only weak peaks.

A quantitative comparison of the amounts of these structures can be seen in Table 4. Except for the primary amide structure, the UV exposure results in a much greater amount of the structures than does heat aging. However, the longer/lower temperature aging is rapidly approaching the 10 day UV exposure conditions. Our hypothesis is that the aldehydes, formamides, and the olefinic structures are formed under both conditions but degrade significantly more quickly at higher temperatures to thermally stable structures (such as methyl groups).

Table 4. Integrated Peak Areas of Various Chemical Structures[a]

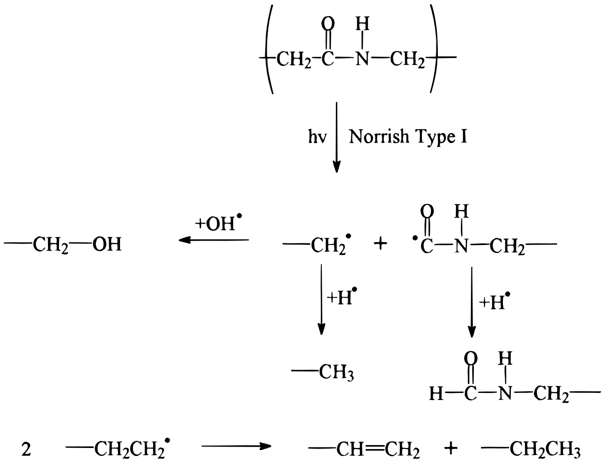
	Vydyne 21 (control)	5 day UV exposure	10 day UV exposure	3 days at 125 °C	3 days at 150 °C	17 days at 90 °C
% methyl	0.00	1.24	1.45	0.08	0.26	0.50
% aldehyde	0.00	0.13	0.11	0.04	0.02	0.10
% formamide	0.00	0.58	0.67	0.10	0.16	0.51
% olefinic end	0.00	0.22	0.27	0.00	0.00	0.15
% amide NH_2	0.11	0.09	0.10	0.10	0.10	0.27
% OCH (80 ppm)	0.00	0.43	0.51	0.00	0.00	0.38
% 7.4 ppm	0.00	0.05	0.05	0.00	0.00	0.00
% 7.3 ppm	0.00	0.09	0.06	0.00	0.00	0.00
% 5.8 ppm	0.00	0.31	0.36	0.00	0.00	0.00

[a] Values are area peaks as a percentage of Nylon-6,6 repeat.

Molecular weight determination was also performed on the Nylon-6,6 pellets control and the various heat-aged samples. The results are shown in Table 3. Unlike the UV exposure case, the changes in molecular weight are relatively minor. The number average (M_n) and weight average (M_w) molecular weights do exhibit a decrease and the M_z value does increase, but in all cases the differences are much smaller than in the UV exposure case. This is consistent with the fact that the heat-aging process produces a much smaller amount of degraded structures than does the UV exposure (Table 4). Once again, a minor amount of cross-linking is occurring as witnessed by the increase in the M_z value.

Reaction Mechanisms

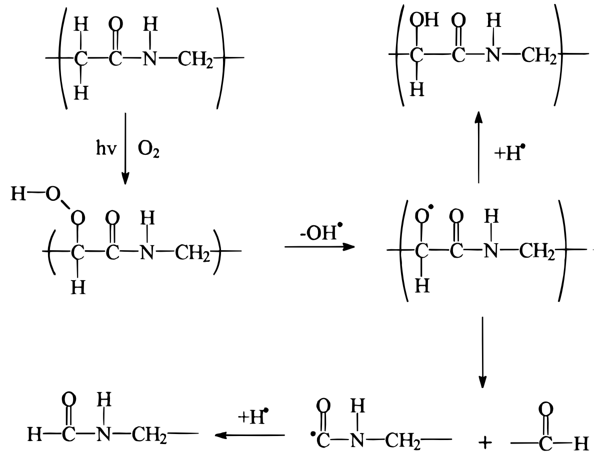
The advantage of our approach to Nylon-6,6 degradation is that it allows us to probe much more precisely the chemical microstructure upon degradation. A review of the data in Tables 2–4 is very informative. Table 2 indicates that there are significant differences in UV and heat degradation. UV degradation results in an increase in carboxylic acid ends and a decrease in amine ends, while heat aging consumes both types of end groups. Table 3 indicates that the main reactions in UV degradation are chain scission and not cross-linking, as the molecular weight values are dropping dramatically upon UV exposure. This is the opposite of heat aging, which produces (after sufficient temperature and/or time) a cross-linked material (as observed in the 175 °C/3 day heat-aged sample). Table 4, however, indicates that the overall reactions are not radically different. Both heat aging and UV degradation produce an increase in methyl, aldehyde, formamide, olefinic end, and OCH; the main difference is that UV exposure produces a larger amount of these structures than does heat aging. It is significant to note that lower temperature/longer times produce significantly more degradation structures than higher temperature aging. Additionally, only low-temperature aging (as opposed to higher temperature aging) produces olefinic and hydroxyl structures. This suggests that the aldehydes and formamides are indeed formed in greater quantities than observed and are thermally degraded during the process. Thus, we propose a more general mechanism to account for the initial degradation products, though the final products depend on the degradation conditions (i.e., high-temperature heat aging degrades some of the initial structures). The reaction mechanisms shown below explain the formation of formamides, aldehydes, methyl, and olefinic groups. These mechanisms are based on the Norrish Type I cleavage of the methylene group next to the carbonyl:



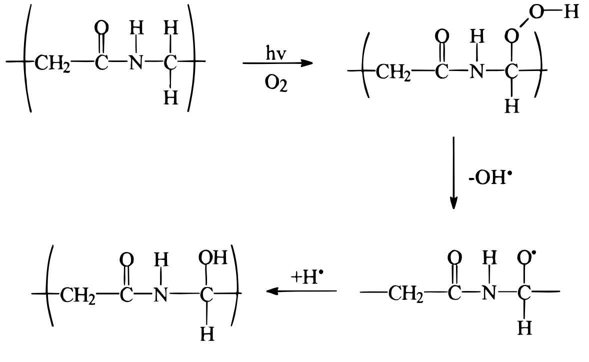
This explains the formation of aldehydes, formamides, and hydroxyls adjacent to the carbonyl group.

The Norrish Type I reaction involving cleavage of the methylene–amide nitrogen bond would produce terminal amide groups, which are not observed for either the UV degradation or heat aging.

Photooxidation of the methylene adjacent to the amide nitrogen can also occur:



The methylene group adjacent to the nitrogen can also undergo photooxidation:



The photoxidation mechanisms also account for the formation of aldehydes, formamides, and amide-adjacent hydroxyl groups. The above reaction mechanisms are consistent with those proposed by earlier workers.[12–18]

Amide bond scission (a bond between the carbonyl and amide nitrogen) has been proposed by some previous investigators. This would result in the formation of amine end groups, which is clearly contradictory to our data in Table 2 for both UV degradation and heat aging.

Conclusions

UV exposure and heat aging of Nylon-6,6 degradation was studied using several 1-D and 2-D NMR techniques. Degradation induced by UV exposure in air resulted in a variety of chain scission reactions, all of which were oriented around the amide groups. The dominant structure in all cases was an *n*-alkylmethyl group. UV exposure also resulted in aldehyde, formamide, and vinylic structures from chain scission and varying amounts of hydroxyl structures. Higher temperature heat aging in air at 125 and 150 °C resulted in the formation of terminal methyl groups in addition to formamide and aldehyde structures. Heat aging at lower temperatures (90 °C) in air also produced methyl groups, formamides, and aldehydes in addition to OCH and terminal vinyl structures. Low-temperature heat aging also produced small amounts of as yet unassigned structures which were not observed in UV exposure or higher temperature heat aging. A detailed evaluation of degradation mechanisms in the literature for applicability to the structures observed in our work was conducted.

Reaction mechanisms were proposed to account for the degradation products.

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