Macromolecules **2000,** *33,* 5655−5664

Resonance Raman Studies of Photoinduced Decomposition of Nylon-6,6: Product Identification and Mechanistic Determination

Hiroshi Matsui, Steven M. Arrivo, and James J. Valentini*

Department of Chemistry, Columbia University, New York, New York 10027

Joseph N. Weber

DuPont Experimental Station, Wilmington, Delaware 19880

Received December 14, 1999; Revised Manuscript Received May 8, 2000

ABSTRACT: We report observation of an enal product of the decomposition of both nylon-6,6 and a nylon-6,6 model compound, *N,N*-hexamethylenebis(hexamide), upon 266 nm pulsed UV laser irradiation of these amides. The product is identified by UV resonance Raman spectroscopy, which shows characteristic band frequencies and intensities of the C═C and C═O stretches of the enal. The vibrational assignment and product identification are supported by experiments with ^{15}N-labeled nylon-6,6. Degradation and spectroscopic characterization under $^{16}O_2$, $^{18}O_2$, and N_2 show that the degradation channel leading to the enal requires molecular oxygen and thereby indicate an oxidative mechanism. The product resonance Raman intensities are directly proportional to the number of photons incident on the sample, consistent with a direct photooxidative process, rather than a thermal−oxidative one with the laser serving as a heat source. We do not observe the enal product when the nylon-6,6 or model compound are simply heated in oxygen-containing atmospheres, except when the heating produces melting.

I. Introduction

Degradation of nylon is accompanied by yellowing and embrittlement which directly influence the performance of the polymer. The rate and course of the degradation are affected by environmental conditions, including the nature of the ambient atmosphere, the intensity and spectral distribution of light to which the material is exposed, the temperature, and the presence of chemical additives and impurities. Because of the industrial importance of nylon and its use in many products, the degradation has been studied extensively for decades in an attempt to reveal the chemical mechanisms of the decomposition. The degradation mechanisms are still not known, but there has been much speculation about them. For one of the major nylon products, nylon-6,6, it has been suggested that, under the action of UV light and oxygen, bond scission is the major decomposition process. Norrish type I and II[1,2] processes are postulated to be initiated by the cleavage of C−C or C−N bonds, and the resultant reactive radicals open various reaction pathways. Extensive and thorough descriptions of these proposed mechanisms have been provided by Pearce[3] and Rossbach.[4]

It is not surprising that no decomposition mechanism has been firmly established, given the complexity of the polymers and the difficulty of isolating and identifying products. Traditional experimental methods of studying polymer degradation measure mechanical properties[5] or viscosity,[5−8] probe the overall kinetics,[9] detect the emitted gaseous species, or look for chemical modification through UV/vis or IR spectroscopy.[4] Many of these do not directly provide identification of chemical species, let alone chemical mechanisms, and those that do identify the chemical species are limited by sensitivity or temporal resolution.

Here we describe the application of a quite sensitive spectroscopic probe of the chemical species resulting from polymer degradation, UV resonance Raman scattering, that provides for chemical species identification from both characteristic vibrational structure and electronic spectra. While the inelastic light scattering of the Raman effect is quite inefficient, it is dramatically enhanced whenever the excitation laser wavelength is tuned into, or even near, an electronic absorption band of a molecule.[10] When the excitation light is in such resonance, the Raman spectrum becomes dominated by vibrational bands that are part of the chromophore responsible for the electronic absorption, and the spectrum thus both simplifies and becomes even more characteristic. Resonance Raman spectroscopy combines both vibrational and electronic spectroscopies and is in effect a two-dimensional spectroscopy. The vibrational spectrum at a particular excitation wavelength provides the first dimension. The excitation spectrum, the intensity of each vibrational band as a function of the wavelength of the light used to excite the Raman spectrum, provides the second. Since most molecules have resonance Raman enhancement in the UV, this spectroscopic approach is quite general, though of course not universal.

Resonance Raman spectroscopy is particularly promising for study of the degradation of nylon and other polymers in which the possible degradation products are less saturated and more conjugated than the polymers themselves and thus likely to show strong resonance Raman enhancement at UV and near-UV wavelengths at which the polymers themselves have much smaller enhancement of the Raman scattering. This differentiation will enhance the intensity of the vibrational bands of the products relative to the vibrational bands of the much more abundant polymer and make it easier to observe and identify the products. The resonance enhancement also increases the absolute sensitivity of detection, making it easier to detect the products. The

---

* To whom correspondence should be addressed. FAX 212-932-1289; e-mail jjv1@chem.columbia.edu.

10.1021/ma9920947 CCC: $19.00

results we report here demonstrate these advantages.

Because of significant resonant Raman enhancement, we observe a Raman spectrum of a product of nylon-6,6 and *N,N*-hexamethylenebis(hexamide), a nylon-6,6 model compound, when the materials are degraded by irradiation with laser pulses of 266 nm UV light in an atmosphere containing molecular oxygen. The presence of vibrational bands in the Raman spectrum that are associated with C=C and C=O stretches, along with the excitation spectrum for these bands, allows us to identify the product as an enal. The product is not formed if the polymer is irradiated in an N_2 atmosphere, so the degradation must be oxidative.

Our experiments do not unambiguously reveal whether the degradation is directly photooxidative or whether the UV irradiation simply heats the sample and promotes a thermal−oxidative route. However, we find that the intensity of the Raman signal from the degradation product is linear in the number of photons incident on the sample, a behavior consistent with a photoprocesses and inconsistent with a thermal one. If we directly heat the sample in oxygen-containing atmospheres, we do not observe the product, except in the case that we heat the model compound above its melting point for several minutes. A consideration of the energy deposition in the sample by the pulsed laser shows that the temperature rise that could be produced by laser heating is too small to be significant. Thus, we believe that the mechanism is a photooxidative one.

II. Experiment

The Raman apparatus used in these studies is similar to that employed in related experiments in this lab and will be described only briefly here.[11−13] A Nd:YAG laser (Continuum NY81C) is the light source for the experiments, both for the UV-laser-induced degradation and for the Raman spectroscopy. The Nd:YAG fourth harmonic at 266 nm effects the degradation. This and the Nd:YAG third harmonic at 355 nm are used for exciting the Raman scattering. Other UV wavelengths are generated by Raman shifting the 266 and 355 nm harmonic outputs of the Nd:YAG in a high-pressure hydrogen cell.

Spectra of powdered solid samples under ambient atmosphere are recorded in a quartz microcell. To record Raman spectra under controlled atmospheres, special sealable quartz cells are used. The Raman scattered light is collected and collimated by a combination of mirrors and lenses and focused into a 1 m monochromator (Spex 14018). The rusultant dispersed Raman spectrum is detected by a UV-enhanced CCD detector (Spex, Spectrum-1) and processed by Spex data acquisition hardware and software.

For the degradation, the 266 nm pulse energy was usually set at 15 mJ, and the laser beam focused to a spot of ≈5 mm diameter on the samples. To check the linearity of the product signal with total photon fluence, other (lower) 266 nm pulse energies were also used. The irradiation with the 6 ns duration pulses at 10 pulses per second was carried out for 2 min. The resonance Raman spectra of the samples were recorded both before and after the degradation-inducing irradiation, with an exposure (1 min) half as long as that for the degradation, at a pulse energy (1.5 mJ) one-tenth as large, with the laser focused to the same ≈5 mm diameter spot.

For studies of degradation of nylon by direct thermal heating without laser irradiation, the quartz cell was heated by a heating tape, which was wound uniformly over the cell surface to provide homogeneous heating. We monitored the sample temperature using a thermocouple installed inside the cell and adjusted the heating current to maintain a set temperature.

The nylon-6,6, *N,N*-hexamethylenebis(hexamide), and ^{15}N-labeled nylon-6,6 were provided by the DuPont Company and used as supplied. Several other chemicals were also needed for the experiments: *trans*-2-heptenal, *trans,trans*-2,4-heptadienal, 1-acethylimidazole, diacetylamide, glutarimide, isobutyramide, 2-hexenoic acid, *N*-methylacetamide, *N,N*-dimethylacetamide, and dimethyl sulfoxide. All of these were obtained from Aldrich and used without further purification. $^{16}O_2$ was obtained from Air Products, $^{18}O_2$ from Matheson Gas Products, and N_2 from All-Weld Products. The stated purities of these gases were 99.6%, 99%, and 99.995%, respectively.

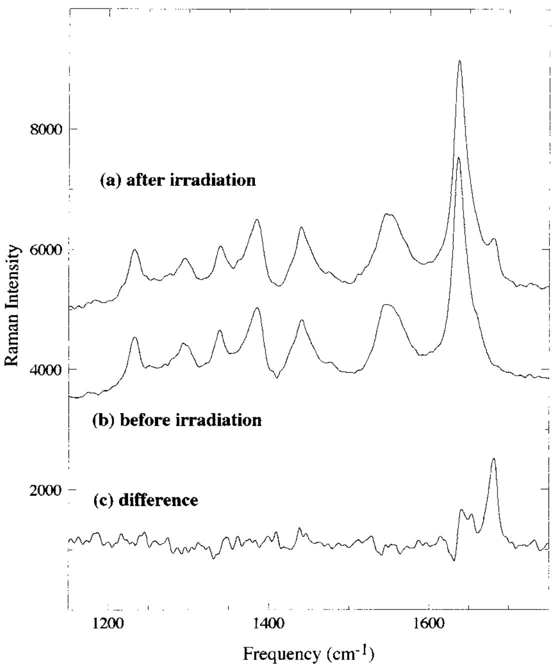


Figure 1. Raman spectra of nylon-6,6. (a) Raman excitation at 266 nm with 1.5 mJ per pulse at 10 pulses per second for 1 min after UV irradiation at 266 nm, with 15 mJ per pulse at 10 pulses per second for 2 min. (b) Raman excitation at 266 nm with 1.5 mJ per pulse at 10 pulses per second for 1 min with no UV irradiation. (c) The difference, spectrum (a) minus spectrum (b).

III. Results and Discussion

a. Degradation of Nylon-6,6 and the Model Compound upon UV Irradiation. Raman spectra of nylon-6,6 excited at 266 nm before and after 266 nm degradation irradiation are presented in Figure 1. While the irradiation that produces degradation and that which is used to record the Raman spectrum are done at the same wavelength, the distinction between “before” and “after” degradation is still clear. The laser pulse energy used for recording the Raman spectrum (1.5 mJ) is only one-tenth that (15 mJ) used to effect degradation, and the duration of exposure of the sample to the laser is only half as long. The conditions used to record the Raman spectrum lead to a level of degradation too small to measure, so the spectrum of the nondegraded sample is obtainable, even though both degradation and Raman spectroscopy are done at the same laser wavelength.

After degradation a band at approximately 1685 cm^{-1} that must be due to a degradation product appears clearly in the Raman spectrum. Except for that band, the before spectrum, (a), and the after spectrum, (b), are both dominated by vibrational bands of the nylon-6,6 polymer. The nylon-6,6 vibrational bands that are characteristic of the amide group are resonance-Raman-enhanced relative to other bands of the polymer, because the 266 nm excitation wavelength is at the long-wavelength edge of the $\pi-\pi^*$ electronic absorption of the amide chromophore.[14−16] These bands are the Am I

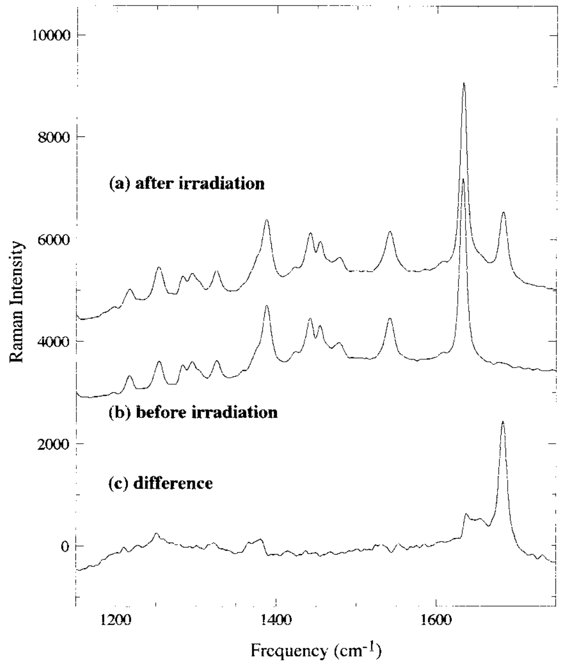


Figure 2. Same as in Figure 1, except for the model compound, *N,N*-hexamethylenebis(hexamide).

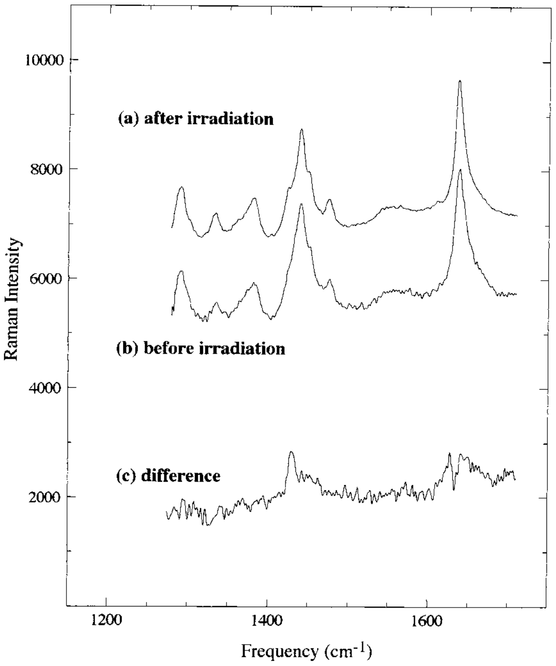


Figure 3. Same as Figure 1, but with Raman excitation at 355 nm.

(C=O stretch), Am II (primarily C−N stretch), and Am III (primarily C−N−H in-plane bend) at 1640, 1550, and 1390 cm^{-1}, respectively.[13,17,−19]

To extract the complete spectrum of the degradation product, it is necessary to take the difference between the before and after spectra. The degradation reduces the intensity of the spectral peaks associated with the nylon-6,6, and so to obtain the product spectrum from the difference of the before and after spectra, it is necessary to scale the spectra to account for this intensity loss. We do this by comparing the intensities of the before and after spectra at peaks between 1300 and 1500 cm^{-1} to compute a scale factor and then multiply the before spectrum by this scale factor before subtracting the before from the after. The scale factor we find is the same no matter what nylon-6,6 spectral peak we choose to compare intensities in the before and after spectra. This "difference" spectrum, (c) in Figure 1, shows not only the 1685 cm^{-1} peak that is evident in the after spectrum but also a peak at 1640 cm^{-1}. The latter does not show up clearly in the after spectrum itself, because it is coincident with the much more intense Am I (C=O) band of the nylon-6,6 polymer.

Similar spectra for the model compound, *N,N*-hexamethylenebis(hexamide), are shown in Figure 2. The difference spectrum, (c), which is the product spectrum, shows the same two prominent peaks at 1640 and 1685 cm^{-1} that the product from the nylon-6,6, does. The ratio of the integrated peak areas of the two bands is the same in both spectra as well, ≈2:1, though the intensity of the 1640 cm^{-1} cannot be established as accurately as we would like due to the overlap with the Am I band of the amide.

For both the nylon-6,6 and the model compound we also recorded spectra with lower UV pulse energies, ranging from 5 mJ up to the 15 mJ used for the spectra presented here. The observed product signal intensities were linear in the pulse energy.

We recorded Raman spectra of the UV-irradiated nylon-6,6 at wavelengths other than 266 nm to determine the excitation spectrum of the degradation product. The degradation-producing irradiation was the same, 2 min with 266 nm light of 15 mJ per pulse at 10 pulses per second, but the before and after Raman spectra were excited at wavelengths other than 266 nm. Figure 3 shows Raman spectra of nylon-6,6 excited by 355 nm light at 1.5 mJ per pulse and 10 pulses per second for 1 min, the same conditions used to record the 266 nm Raman spectra in Figure 1. The spectrum of the polymer after 266 nm UV irradiation is (a), and that before is (b). The product spectrum is the difference between these, again with the before spectrum scaled to account for loss of sample due to the degradation, with the scale factor determined by comparing peak intensities for bands between 1300 and 1500 cm^{-1}. The intensities of the product bands at 1640 and 1685 cm^{-1}, which are clearly seen in the Raman spectrum excited at 266 nm, are so reduced in this 355 nm excitation spectrum that they are not observable.

The same behavior is seen for the product in the model compound degradation. Figure 4 shows 355 nm excited Raman spectra of the model compound, both before and after irradiation, using the same experimental conditions as for the nylon-6,6 spectra in Figure 3. Because of the higher signal-to-noise level obtainable with the model, it is possible to detect the product peaks in the difference spectrum of Figure 4. However, both the 1640 and 1685 cm^{-1} product peaks are much less intense for excitation of the Raman spectrum at 355 nm than at 266 nm.

Comparison of the spectra of Figures 1 and 3 or Figures 2 and 4 reveals the reduction of Raman intensity for the product peaks as the Raman excitation is tuned to longer wavelength. This is a loss in both absolute terms and also relative to the intensity of the amide peaks of the polymer and model. The characteristic amide group bands, the Am I (C=O stretch), Am II (primarily C−N stretch), and Am III (primarily C−N−H in-plane bend) at 1640, 1550, and 1390 cm^{-1}, respectively, also lose intensity as the excitation is tuned

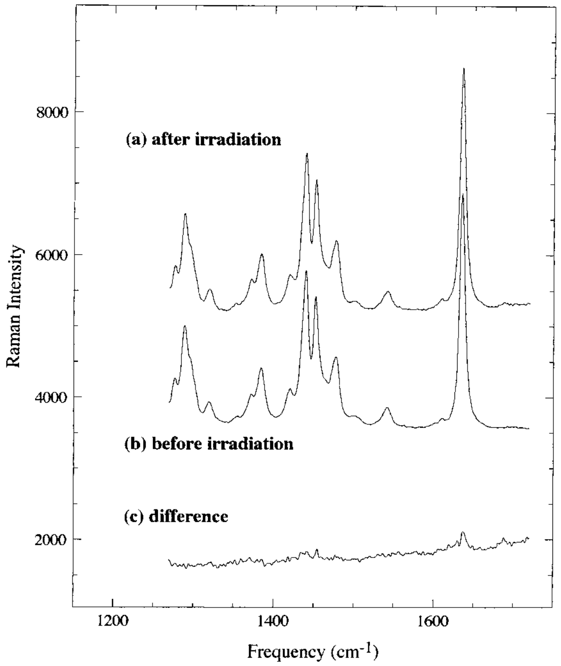


Figure 4. Same as Figure 2, but with Raman excitation at 355 nm.

to longer wavelength and therefore farther from resonance with the $\pi-\pi^*$ electronic absorption of the amide chromophore (vide supra).[14−16] This can be seen by comparing the intensities of the Am I, II, and III bands with those of the non-amide bands around 1440 cm^{-1} in Figures 1−4. However, the degradation product bands lose more intensity between 266 and 355 nm than the amide bands do. This indicates a stronger wavelength dependence of the Raman excitation spectrum for the product and suggests that the product has an electronic absorption with a peak that lies closer to 266 nm than does that of the amide, that is, that the product has an electronic absorption at longer wavelength than the amide itself.

b. Degradation of ^{15}N-Labeled Nylon-6,6 upon UV Irradiation. Measurement of isotope shifts of vibrational bands is a standard approach to assigning the molecular carrier of the bands. Here we used an ^{15}N-labeled nylon-6,6 sample to help in the assignment of the molecular nature of the two bands attributable to degradation product that we see in the Raman spectra of Figures 1−4. We irradiated and probed that sample in the same way that we did for the normal nylon-6,6 sample whose spectra are shown in Figure 1. Figure 5 shows a comparison of Raman spectra from identically processed ^{15}N-labeled, (a), and ordinary ^{14}N-nylon-6,6, (b), with irradiation and Raman spectroscopy both using 266 nm UV light. The ^{15}N-labeled and ordinary ^{14}N sample spectra are subtracted to yield the difference spectrum, (c).

Since both (a) and (b) are from irradiated samples, the difference spectrum (c) is not the spectrum of the product but rather gives the *change* in the product spectrum when ^{15}N is substituted for ^{14}N. The spectra show that there is no shift in the position of the 1685 and 1640 cm^{-1} product bands within the 1 cm^{-1} precision of our measurements. Neither the spectrum of the ^{15}N-labeled sample nor the difference spectrum shows any new product peaks or shifting of product peaks. There are peak shifts, but these are associated with isotope shifts in the amide bands of the nylon-6,6 itself. These shifts are most clearly revealed by the dispersive peaks in the difference spectrum, around 1640 and 1540 cm^{-1}, which have previously been assigned to the Am I and II vibrations, and at 1230 cm^{-1}, another amide group band.[13,17−19] That these are indeed associated with the nylon, not the product, is evident from the Raman spectra of Figure 6, which show the spectrum of the ^{15}N-labeled, (a), and ordinary ^{14}N-nylon-6,6, (b), samples before irradiation, and their difference, (c). The dispersive peaks are the same in the difference spectra of both Figures 5 and 6.

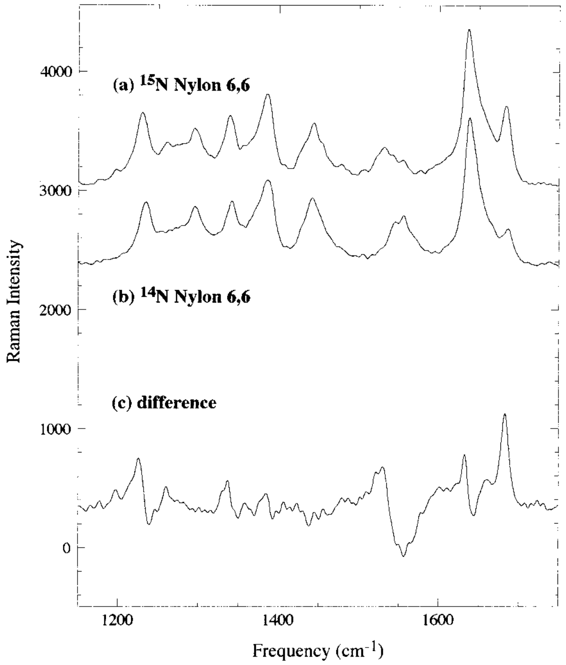


Figure 5. Resonance Raman spectra of UV-irradiated nylon-6,6: (a) ^{15}N-labeled nylon-6,6 sample; (b) ordinary ^{14}N-nylon-6,6 sample; (c) the difference, spectrum (a) minus spectrum (b).

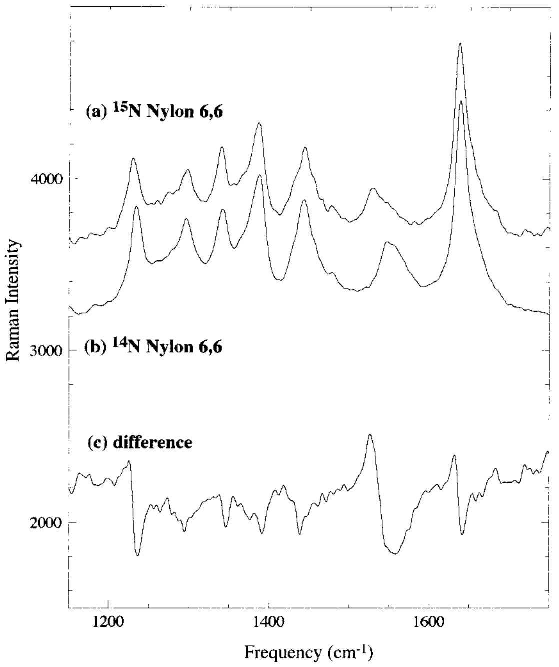


Figure 6. Same as Figure 5, but for samples before UV irradiation.

Substitution of ^{15}N for ^{14}N shifts amide bands to lower frequency when the vibrational normal modes corresponding to a band has an effective mass that includes a contribution from the mass of the nitrogen. In the polymer and model compound the biggest shift should be observed for the Am II, which is primarily the C−N stretch. That band would thus have a frequency with the biggest dependence on nitrogen mass, and that is what is observed. The Am II shifts to lower frequency by 20 cm^{-1}, while the Am I, which is predominantly C═O stretch, shifts by only 2 cm^{-1}. For comparison, a C−N diatom with a vibrational frequency of 1550 cm^{-1} (the Am II frequency) would shift by 24 cm^{-1} upon ^{15}N for ^{14}N substitution.

Given the elemental composition of nylon and the model compound, vibrational bands around 1600−1700 cm^{-1} would have to be associated with stretch vibrations of C═C, C═O, or C═N groups. The absence of any observable shifts for the 1640 and 1685 cm^{-1} product bands when we substitute ^{15}N for ^{14}N indicates that neither of these bands is a C═N vibration. As we describe in the next subsection, this negative evidence for assignment as C═N is also supported by positive evidence that the 1685 cm^{-1} band is due to C═O.

Although there are no vibrational frequency shifts for the product bands in the degradation of the ^{15}N-labeled and ordinary ^{14}N samples, the difference spectrum of Figure 5 does not show a null at 1685 cm^{-1}, because the intensity of that peak is not the same in the spectra of the ^{15}N-labeled and ordinary ^{14}N samples. This is not surprising, in that we have noted variation in the product peak intensity among different nylon-6,6 samples. The variation may reflect variations in morphological characteristics of the samples.

c. Degradation of Nylon 6,6 upon UV Irradiation under Controlled Atmospheres. An oxidative degradation via chain scission has been suggested as the first step in the nylon degradation mechanism.[2] This mechanism requires oxygen from the ambient atmosphere. We addressed this possibility and took another step in the identification of the degradation product we observe, by examining the resonance Raman spectra of nylon-6,6 and model compound samples irradiated in controlled atmospheres. The spectra of Figures 1−6 were taken on samples exposed to air. The spectra of Figures 7−9 which follow were obtained in sealable cells with samples contained in pure $^{16}O_2$, $^{18}O_2$, or N_2.

Figure 7 presents a comparison of resonance Raman spectra of nylon-6,6 irradiated under $^{16}O_2$ and $^{18}O_2$. In each case the irradiation consisted of 2 min exposure to 15 mJ pulses of 266 nm laser light at 10 pulses per second, just as with all the other irradiated samples. In this figure (a) is the spectrum under $^{18}O_2$, (b) gives that under $^{16}O_2$, and (c) is the difference between them. Since both (a) and (b) are spectra of irradiated samples, the difference spectrum is not the spectrum of the product, but the *change* in it when the isotopic composition of the ambient molecular oxygen atmosphere is changed. The difference spectrum is very clear. It shows loss of product Raman intensity at 1685 cm^{-1}, and a concomitant increase of product Raman intensity around 1640 cm^{-1}, but no new peaks at Raman shifts below 1640 cm^{-1}.

This shift in intensity is entirely consistent with the identification of the 1685 cm^{-1} band as due to a C═O vibration. A C═O diatom with a frequency of 1685 cm^{-1} for ^{16}O would show an isotope shift of 42 cm^{-1} upon ^{18}O for ^{16}O substitution. The difference spectrum of Figure 7 shows an isotope shift of ≈40 cm^{-1}. Since carbonyl vibrational normal modes usually have close to pure C═O stretch local mode character, an isotope shift close to this diatomic benchmark value should be observed if the 1685 cm^{-1} band is from a carbonyl. The difference spectrum also shows that there is no gain in intensity at any frequency lower than 1640 cm^{-1}. This implies that the 1640 cm^{-1} product band is not associated with a normal vibrational mode involving any O atom motion.

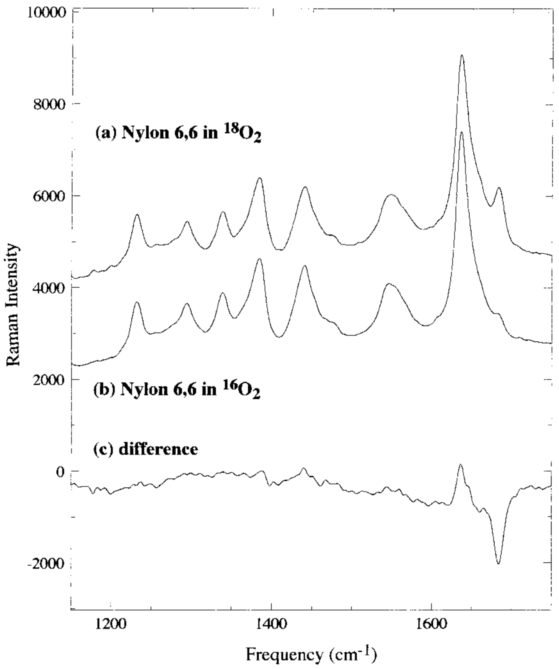


Figure 7. Resonance Raman spectra of UV-irradiated nylon-6,6: (a) nylon-6,6 sample in $^{18}O_2$; (b) nylon-6,6 sample in $^{16}O_2$; (c) the difference, spectrum (b) minus spectrum (a).

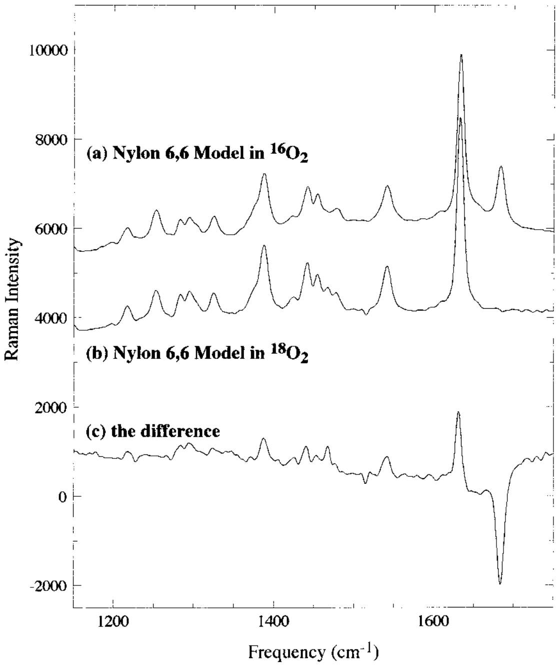


Figure 8. Same as for Figure 7, but for the model compound.

The same controlled experiments under $^{16}O_2$ and $^{18}O_2$ were carried out for the model compound, and the results are shown in Figure 8. As with the nylon-6,6

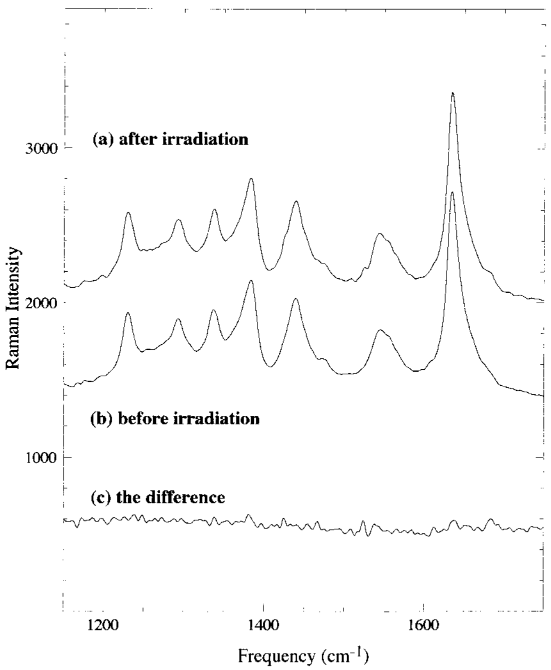


Figure 9. Resonance Raman spectra of UV-irradiated nylon-6,6 in N_2: (a) after irradiation; (b) before irradiation; (c) the difference, spectrum (a) minus spectrum (b).

polymer, the difference spectrum here shows product Raman spectral intensity loss at 1685 cm^{-1} and an increase at 1640 cm^{-1} and nothing else.

The spectral changes (or lack thereof) seen in the ^{15}N-labeled and $^{18}O_2$ atmosphere samples relative to their normal isotopic variants imply that neither product peak is connected with a vibrational normal mode of a functional group that contains nitrogen. They show that the 1685 cm^{-1} peak is that for a vibration of a functional group that does involve an O atom and that the 1640 cm^{-1} peak is not associated with an N-atom-containing or O-atom-containing functional group normal mode. This behavior, combined with the vibrational frequencies of the bands, implies that the product contains both a C═C bond and a C═O bond, with the former associated with the 1640 cm^{-1} band and the latter with the band at 1685 cm^{-1}.

These results show not only the presence of a C═O-containing functional group in the product but also the origin of the oxygen in that carbonyl as being with the atmosphere surrounding the polymer. That is, they show an oxidative mechanism for the degradation. Further evidence for this mechanism comes from our spectra of nylon-6,6 and model compound samples irradiated with UV light in an atmosphere of N_2. The nylon-6,6 spectra are shown in Figure 9. The difference spectrum is almost completely flat. There is only a small amount of intensity at 1685 cm^{-1} and perhaps at 1640 cm^{-1}. Since the nylon-6,6 we used was synthesized in the presence of oxygen and was exposed to air for an extended period before we used it for these experiments, it could have some molecular oxygen dissolved in it, and this dissolved oxygen could be the source of the small amount of product formed. The before irradiation spectra in Figures 1 and 9 are almost identical. This indicates that the presence of atmospheric oxygen has little if any effect on the polymer itself before photooxidation occurs.

The nylon-6,6 in N_2 results are singular in another way. The difference between the Raman spectral intensities after irradiation under N_2 as compared to before irradiation is much smaller than the before−after difference observed for samples irradiated in air and in pure oxygen. This further confirms the absence of degradation in the absence of molecular oxygen.

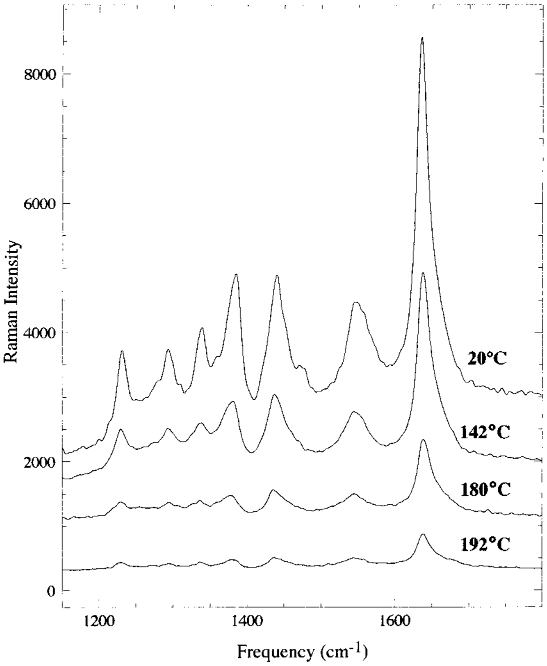


Figure 10. Resonance Raman spectra of nylon-6,6 after heating for 1 min in $^{16}O_2$ to various temperatures.

d. Thermal Degradation of Nylon-6,6. We have used resonance Raman scattering also to look for product upon direct thermal heating of nylon-6,6 and the model compound. Figure 10 shows the 266 nm excitation spectra of polymer samples that have been heated to temperatures as high as 465 K for 1 min in a sealed cell under an atmosphere of molecular oxygen and then cooled back down to room temperature. The heating results in loss of Raman intensity of vibrational bands assignable to the polymer, and this reveals the decomposition of the polymer. However, we do not see the appearance of the vibrational bands at 1640 and 1685 cm^{-1} that we find upon UV laser irradiation. Nor do we see any product bands when the model compound is heated to temperatures just below its melting point, as evidenced by the spectra of Figure 11, for samples heated for various times to 427 K.

The only cases in which thermal heating produces detectable amounts of product occur when we heat the model compound above its melting point for several minutes. The spectra of Figure 12 show 266 nm Raman spectra of the model compound after it has been heated to 465 K for 1−4 min and then cooled to room temperature. The 1680 cm^{-1} vibrational band characteristic of the product is apparent in the spectra taken after an additional 3 min of heating at this above-the-melting-point temperature. This suggests that the product we observe can be produced by thermal degradation under extreme conditions but is not produced by a thermal mechanism upon laser irradiation.

A simple consideration of the possible heating by the laser shows that a thermal process driven by the laser irradiation is highly unlikely. The laser is hardly focused, and very little of the UV light can be absorbed because the absorption coefficient of the polymer and

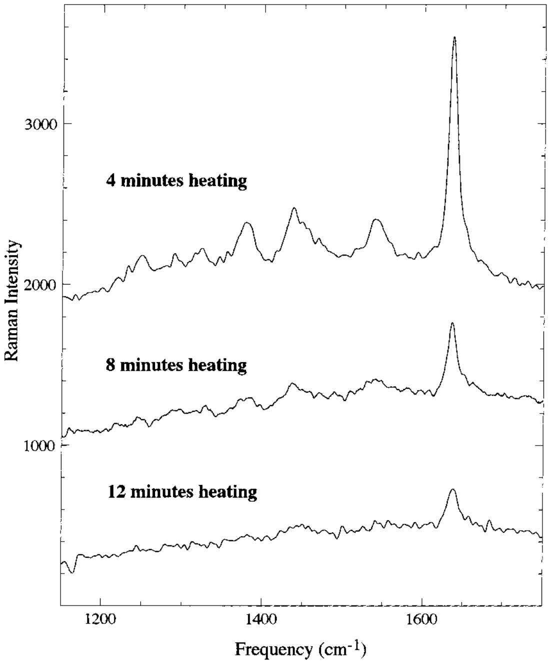


Figure 11. Resonance Raman spectra of the model compound after heating in $^{16}O_2$ to 427 K for various times.

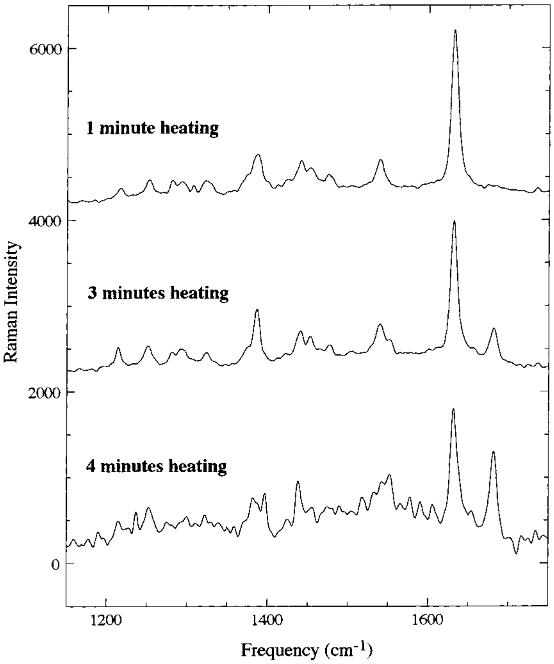
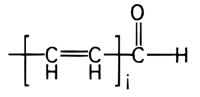
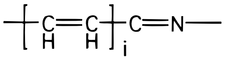
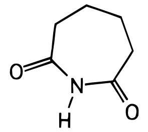
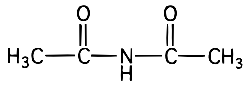
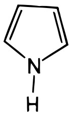


Figure 12. Same as Figure 11, but for samples heated to 465 K.

Table 1. Proposed Degradation Products of Nylon-6,6

Proposed Nylon 6,6 degradation products	Examples	References
unsaturated carbonyls		3,26-28
ketoimines		4
cyclic ketoimides		29
ketoimides		30
pyrrolyls		31

model compound are both very small at 266 nm, so the energy deposition per unit volume is very small. A calculation of the temperature rise using the irradiation conditions, and the heat capacity of the model compound indicates that a temperature rise of less than 10 K is possible. Even the prolonged heating of the nylon-6,6 or the model compound at a temperature 10 K above ambient temperature is insufficient to produce measurable product intensity.

More compelling than this calculation is the observation (vide supra) that the product band intensities are linear in the photon fluence. A thermally activated process would show a nonlinear dependence, i.e., Arrhenius behavior. Thus, we believe that the UV irradiation effects a photooxidative degradation of the polymer.

e. Identification of the Product. We recorded the resonance Raman spectra of compounds that are likely photooxidative products. The development of a library of comparison spectra is required because there are no atlases of resonance Raman spectra, as there are of ordinary Raman or IR spectra. There is good reason for this. First, the number of UV resonance Raman spectra that have been recorded and reported is relatively small. More important, the resonance Raman spectrum is strongly excitation wavelength dependent (see Figures 1−4), and so there is no single resonance Raman spectrum for any species; there are an infinite number.

Classes of compounds that have been proposed as products of the degradation are given in Table 1, along with references to the literature describing the reasoning that suggests such products. The putative products include unsaturated carbonyls, ketoimines, cyclic ketoimides, ketoimides, and pyrrolyls. To represent the ketoimides and pyrrolyls, we selected diacetylamide, glutarimide, and 1-acethylimidazole. Resonance Raman spectra of these compounds excited at 266 nm are shown in Figure 13. Each shows too many peaks or peaks at frequencies that do not match those of the product we observe.

We also recorded the resonance Raman spectra of the conjugated carbonyls, *trans*-2-heptenal and *trans,trans*-2,4-heptadienal. The resonance Raman spectra of these are shown in Figure 14. The *trans,trans*-2,4-heptadienal spectrum shows only one intense peak, at 1635 cm^{-1}, for 266 nm Raman excitation. For Raman excitation at 355 nm a weaker 1660 cm^{-1} band also appears in the spectrum. The intensity of the 1635 cm^{-1} band is greater by almost a factor of 10 for excitation at 355 nm as compared to excitation at 266 nm. Neither the relative peak intensities nor the Raman excitation wavelength dependence matches those in the Raman spectrum of the product we observe.

For the other unsaturated carbonyl, 2-heptenal, there is a very good match. For 266 nm Raman excitation there are two strong transitions, at 1635 and 1680 cm^{-1},

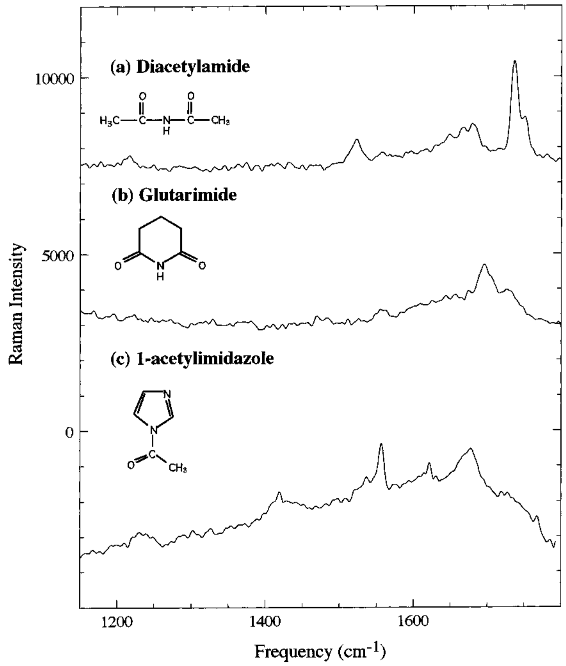


Figure 13. Raman spectra of ketoimides and pyrrolyls excited at 266 nm.

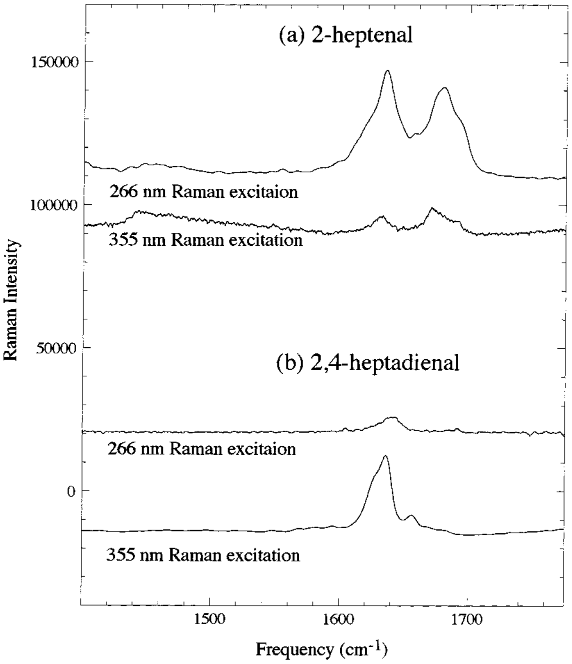


Figure 14. Raman spectra of (a) 2-heptenal and (b) 2,4-heptadienal excited at 355 and 266 nm.

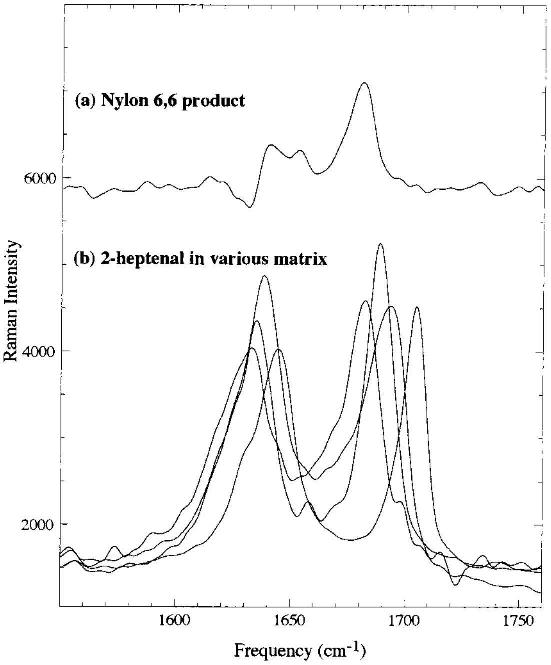


Figure 15. Comparison of the 266 nm Raman spectrum of the nylon-6,6 degradation product (a), with 266 nm Raman spectra of 2-heptenal (b) in various solvents.

very close to the peak positions in the product. These peaks are also present in the Raman spectrum recorded at 355 nm, but their intensity is much reduced from that at 266 nm, just as is the case with the degradation product. The 1635 and 1680 cm^{-1} peaks have been assigned as C=C and C=O stretch modes, respectively,[20,21] which is consistent with our ^{16}O, ^{18}O, ^{14}N, and ^{15}N spectra of the product. While the vibrational band positions agree well with the two product peaks at 1640 and 1685 cm^{-1} observed in the Raman spectra for UV-irradiated nylon-6,6 and nylon-6,6 model, it is clear that the observed relative intensities of the two peaks is not the same in the 2-heptenal spectrum. The lower frequency peak is of greater relative intensity, while in the product spectra it is of lower relative intensity.

Care has to be exercised in the comparison of both the frequencies and intensities between Raman spectra of the neat 2-heptenal and the spectral intensities and frequencies of the product in nylon-6,6 or the model compound. Spectral intensities and frequencies are solvent- or matrix-dependent, so even if the 2-heptenal is the product, we do not expect the spectrum of the neat compound to match exactly the spectrum of 2-heptenal in a matrix of nylon-6,6. We have investigated the solvent dependence of the 2-heptenal spectrum, putting it in solution with solvents that should mimic the chemical environment, if not the physical one, of the product in the nylon-6,6 and model. Figure 15 shows 266 nm resonance Raman spectra of 2-heptenal in hexane, *N*-methylacetamide, *N*,*N*-dimethylacetamide, and dimethyl sulfoxide, each at 1:30 by volume. The Raman spectrum of the solvent has been subtracted out. The peak position of the C=C band varies from 1630 to 1645 cm^{-1}, while the C=O falls in the range 1680−1705 cm^{-1}. The relative intensities of the two peaks vary as well. Comparison of the degradation product spectrum, also plotted in Figure 13, shows that the range over which these C=C and C=O bands of 2-heptenal can vary encompasses the observed band positions for the product.

The best agreement of the 2-heptenal spectra with that of the product occurs with *N*,*N*-dimethylacetamide as the solvent. The agreement is better than that in *N*-methylacetamide, which might appear to be a better mimic of the polymer, since both it and the polymer are trans-configured secondary amides, while *N*,*N*-dimethylacetamide is a tertiary amide. However, in previous studies[13] we have shown that the resonance Raman spectra of nylon polymers and model compounds are more like that of *N*,*N*-dimethylacetamide than like that of *N*-methylacetamide, so this is not surprising here.

Spectral intensities and frequencies are concentration-dependent as well when the solutions do not

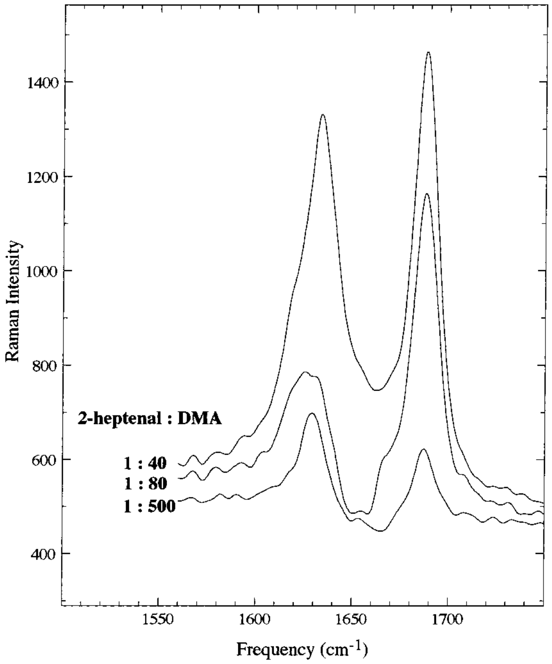


Figure 16. Raman spectra of 2-heptenal in *N*,*N*-dimethylacetamide at different concentrations, all for excitation at 266 nm.

approximate ideal behavior at infinite dilution. We do not know the concentration of the product in the polymer, but whatever it is, the behavior is likely to be nonideal. So, we also examined the concentration dependence of the 266 nm resonance Raman spectrum of 2-heptenal, choosing *N*,*N*-dimethylacetamide as the solvent. The results are shown in Figure 16, and they do indicate a clear concentration variation.

The closest match between the Raman spectra of 2-heptenal in *N*,*N*-dimethylacetamide solution and that of the degradation product occurs for 2-heptenal in *N*,*N*-dimethylacetamide at 1:80 by volume. The Raman spectrum of that solution for both 266 and 355 nm excitation is shown in Figure 17, along with the corresponding spectra of the product in nylon-6,6 and the model compound. The matching of peak positions, relative intensities, and excitation wavelength dependence are all quite good.

We believe that this offers quite sound identification of an unsaturated, conjugated carbonyl, an enal, as the product. Since the resonance Raman spectra show only the vibrational bands characteristic of the C═C and C═O groups, we cannot identify a particular unsaturated carbonyl as the product.

Since further oxidation of the enal could proceed[4,22,23] to produce carboxylic acids, we recorded Raman spectrum of 2-hexenoic acid as shown in Figure 18. The strong Raman scattering in the 355 nm excitation spectrum disagrees with what we observe for the product in nylon-6,6 and the model. Thus, it appears that under our degradation conditions the enal is not further oxidized to a carboxylic acid.

IV. Discussion

There are two different mechanisms that could lead to products containing the C═C and C═O groups that our observed degradation product has. These mechanisms are presented in Figure 19. The first of these, a proton-transfer mechanism, results in formation of a product with a C═N bond as well. The other scheme involves oxidative degradation to produce an enal and a primary amide via chain scission. All the evidence we have supports the second of these.

First, we have established that an enal is the carrier of the resonance Raman spectrum we observe. Extensive comparison of the resonance Raman spectrum and Raman excitation function of the product indicates a good match with only one class of compounds, the unsaturated, conjugated carbonyls. While no such search can be completely exhaustive, we have considered and examined a very large number of compounds that are

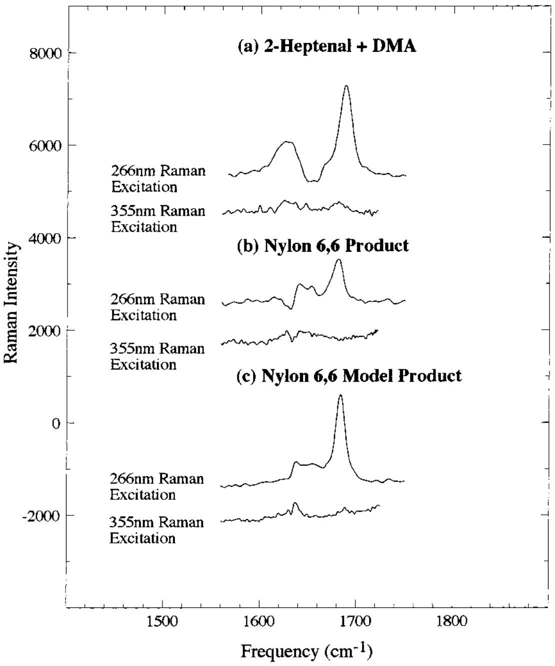


Figure 17. Comparison of the 266 and 355 nm Raman spectra of 2-heptenal in *N*,*N*-dimethylacetamide (a), with the 266 and 355 nm Raman spectra of the nylon-6,6 degradation product, (b), and the nylon-6,6 model degradation product, (c).

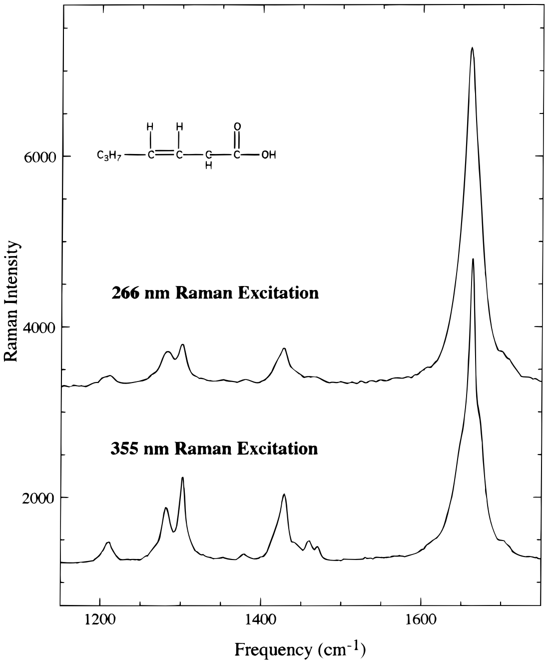
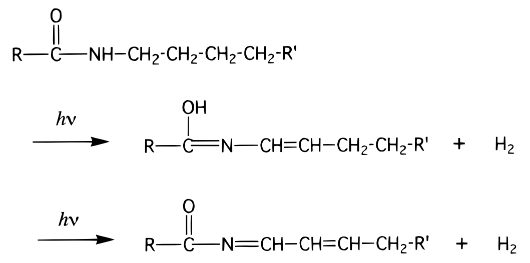


Figure 18. Raman spectra of 2-hexenoic acid, excited at 266 and 355 nm.



Scheme 2. Chain Scission

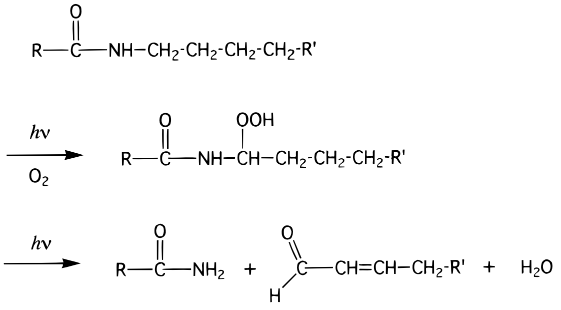


Figure 19. Proposed schemes for the degradation of polyamides.

possible products. No other compound gives a Raman spectrum that comes close to matching that of the product.

Second, we have shown that the product is formed by an oxidative process, since the carbonyl in it acquires its oxygen content from molecular oxygen in the environment of the polymer, not from the amidic oxygen of the polymer itself. Comparison of product Raman spectra from degradation in atmospheres of $^{16}O_2$ and $^{18}O_2$ indicates an isotope shift of the correct sign and magnitude for a $C{=}^{16}O$ versus $C{=}^{18}O$ product. Studies in an atmosphere of N_2 reveal no product.

Third, we have shown that there is no C=N group in the product we observe. Degradation studies of ^{15}N-labeled nylon-6,6 show no shifts of any bands in the Raman spectrum, except for those of the polymer itself.

We do not see any Raman spectroscopic evidence for the other product of the chain scission mechanism, a primary amide, but we would not expect to be able to observe this product. The primary amide resonance Raman spectrum is very similar to that of the polymer, a secondary amide, and the degree of resonance enhancement will be comparable for the polymer and the primary amide degradation product. So, the Raman spectrum of the primary amide product will be hard to observe. Also difficult to observe would be monoalkylalkenes, $R-CH=CH_2$, that have been suggested[3,23] to occur in polyamide degradation via a Norrish type II mechanism. The relative resonance enhancement of the Raman bands of these molecules will not be large compared to that of the amide itself. Further, the C=C stretch frequencies in the monoalkyl alkenes are 1638–1650 cm^{-1},[24] overlapping the Am I band of the polyamide itself. So, these products will be observable only at high levels of degradation.

It appears that the product we observe is formed through a photooxidative process, not a thermooxidative one. Though the product is the result of photoexcitation upon 266 nm laser excitation, this does not demonstrate that reaction involves a photoexcited species. The energy supplied by the laser could simply go to heating the sample. Photoabsorption, leading to production of an excited electronic state of the polymer, could be followed by energy transfer and internal conversion,[2] dissipating the excitation energy as heat in the sample. However, the laser pulse energies used in the experiment are too small to produce any meaningful macroscopic heating of the sample. More importantly, the product yield is linear in the incident photon fluence, a behavior consistent with a photooxidative mechanism, but not with an activated thermooxidative one. Further, we do not observe the enal product in samples that are directly thermally heated under atmospheres containing molecular oxygen, except when the samples are heated above the melting point.

Acknowledgment. This research is supported by the DuPont Company.

References and Notes

(1) Hawkins, W. L. *Polymer Degradation and Stabilization*; Springer-Verlag: New York, 1984.
(2) Rabek, J. F. *Photodegradation of Polymers*; Springer-Verlag: New York, 1996.
(3) Do, C. H.; Pearce, E. M.; Bulkin, B. J.; Reimschuessel, H. K. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2301.
(4) Karstens, T.; Rossbach, V. *Makromol. Chem.* **1990**, *191*, 757.
(5) Schefer, W. *Textilveredlung* **1985**, *20*, 351.
(6) Achhammer, B. G.; Reinhart, F. W.; Kline, G. M. *J. Appl. Chem.* **1951**, *1*, 301.
(7) Head, F. S. *J. Text. Inst.* **1973**, *64*, 608.
(8) Moore, R. F. *Polymer* **1963**, *4*, 493.
(9) Karstens, T.; Rossbach, V. *Makromol. Chem.* **1989**, *190*, 3033.
(10) Ferraro, J. R.; Nakamoto, K. *Introductory Raman Spectroscopy*; Academic Press: New York, 1994.
(11) Triggs, N. E.; Valentini, J. J. *J. Phys. Chem.* **1992**, *96*, 6922.
(12) Triggs, N. E.; Bonn, R. T.; Valentini, J. J. *J. Phys. Chem.* **1993**, *97*, 5535.
(13) Triggs, N. E.; Valentini, J. J. *Isr. J. Chem.* **1994**, *34*, 89.
(14) Kaya, K.; Nagakura, S. *Theor. Chim. Acta* **1967**, *7*, 117.
(15) Kaya, K.; Nagakura, S. *Theor. Chim. Acta* **1967**, *7*, 124.
(16) Neilsen, E. B.; Schellman, J. A. *J. Phys. Chem.* **1967**, *71*, 2297.
(17) Katagiri, G.; Leonard, J. D.; Gustafson, T. L *Appl. Spectrosc.* **1995**, *49*, 773.
(18) Jakes, J.; Krimm, S. *Spectrochim. Acta* **1971**, *27A*, 19.
(19) Zimba, C. G..; Rabolt, J. F.; English, A. D. S. *Macromolecules* **1989**, *22*, 2863.
(20) Freeman, S. K. *Application of Laser Raman Spectroscopy*; John Wiley & Sons: New York, 1974.
(21) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1985.
(22) Sager, B. F. *J. Chem. Soc. (B)* **1967**, 1047.
(23) Sharkey, W. H.; Mochel, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 3000.
(24) Booth, G. H.; Norrish, G. W. *J. Chem. Soc.* **1952**, 188.
(25) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: New York, 1991.
(26) Allen, N. S.; McKellar, J. F.; Wilson, D. *J. Photochem.* **1976**, *6*, 337.
(27) Allen, N. S.; Harrison, M. J. *Eur. Polym. J.* **1985**, *21*, 517.
(28) Fromageot, D.; Roger, A.; Lemaire, J. *Angew. Makromol. Chem.* **1989**, *170*, 71.
(29) Scharf, H. D.; Dieris, C. G.; Leismann, H. *Angew. Makromol. Chem.* **1979**, *79*, 193.
(30) Boasson, E. H.; Kamerbeek, B.; Algera, A.; Krose, G. H. *Recueil* **1962**, *81*, 624.
(31) Herlinger, H. *Lenzinger Ber.* **1974**, *36*, 76.

MA9920947