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Solution ^{17}O NMR study of thermal hydrolysis in nylon 6,6

Todd M. Alam*

Department of Organic Materials, Sandia National Laboratories, Albuquerque, NM 87185-0888, USA

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Abstract

The thermal hydrolysis of nylon 6,6 between 338 and 398 K was investigated using solution ^{17}O NMR spectroscopy. By performing the hydrolysis with isotopically ^{17}O-enriched H_2O, it is possible to easily identify the non-volatile oxygen-containing degradation products formed during the hydrolysis of nylon. For the aging temperature range investigated, the dominant oxygen-containing degradation species are carboxylic acids, consistent with the hydrolytic cleavage of the amide bond. These ^{17}O NMR studies allowed the temperature variation for the hydrolysis of the amide bond in nylon 6,6 to be determined with of the initial rate of carboxylic acid concentration production giving an energy of activation of ~87 ± 1 kJ/mol.

Keywords: NMR; ^{17}O NMR; Hydrolysis

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1. Introduction

The commercial importance of aliphatic nylons has led to considerable research into the degradation and decomposition mechanisms in these materials. This research includes investigations into the biodegradation of polyamides [1,2], thermal and photo-oxidative decomposition of nylons [3–6], cross-linking in polyamides [7], and decarboxylation and deamination in nylon [8,9]. In the presence of water, hydrolysis is the primary decomposition pathway in polyamides leading to the cleavage of the amide bond, and has been investigated using a variety of techniques [5,9–13]. In nylons, there has also been work investigating the increased brittleness that occurs with extensive drying [14,15], and the hydrolysis of nylon 6,6 in supercritical water [16]. At Sandia National Laboratories recent studies involving the degradation of nylon used in parachute systems have revealed that the atmospheric composition during hydrolysis plays a crucial role in the observed rate of degradation [17,18]. Presently, the mechanistic details of these atmospheric effects on nylon hydrolysis remain unanswered.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for the investigation of polymer degradation. Recently, we have demonstrated that solution ^{17}O NMR can be used to study specific questions about the oxidation and hydrolysis mechanisms in a variety of polymer systems. Solution ^{17}O NMR studies have been reported for the thermal oxidative degradation of polypropylene, nitrile rubber, ethylene–propylene–diene (EPDM) rubber, pentacontane, polyisoprene, and hydroxy-terminated polybutadiene (HTPB)/isophorone diisocyanate (IPDI) based polyurethane rubber [19–22]. The radiolytic oxidation of pentacontane and polyisoprene [23], the hydrolysis of estane [24], and the radiolytic hydrolysis of polysiloxane composites [24,25] have also been reported. These ^{17}O NMR studies rely on the selective introduction of the ^{17}O isotope (0.037% natural abundance) during the aging process to produce ^{17}O-labeled degradation species. In this paper, these ^{17}O NMR studies are extended to investigate the thermal hydroloysis of nylon 6,6, where the ^{17}O label is introduced during the hydrolysis process via:

$$\text{Nylon } 6,6 \xrightarrow[\Delta]{^{17}\text{O}-\text{H}_2\text{O}(l)} {}^{17}\text{O} - \text{Labeled Hydrolysis Products}$$

This selective introduction of the ^{17}O isotope, allows for the direct identification and quantification of the non-volatile and semi-volatile oxygen containing degradation species, produced and retained in the nylon 6,6 using solution ^{17}O NMR spectroscopy, without interference from the background ^{17}O NMR signal of the unaged or native polymer. These ^{17}O NMR studies also allow individual degradation

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* Tel.: +1-505-844-1225; fax: +1-505-844-9624.
E-mail address: tmalam@sandia.gov (T.M. Alam).

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pathways to be studied through the selective introduction of the ^{17}O isotope. These investigations provide the baseline for future ^{17}O NMR investigations into the effects of different atmosphere compositions on nylon hydrolysis.

2. Experimental

The nylon 6,6 strap/ribbon samples were obtained in 1989 from Bally Ribbon Mills (Bally, PA), stored indoors, and were used without further sample modification or drying. The nylon samples were hydrolytically aged by placing appropriate weights of cut nylon in borosilicate glass vials suspended above a saturated K_2SO_4/H_2O salt solution inside sealed ampoules under air. The salt solutions were prepared using isotopically labeled (28.0% ^{17}O) $H_2^{17}O$ (Isotec, Miamsburg, OH). The sealed ampoules were then aged at different temperatures for varying lengths of time. A small portion of the nylon sample was removed at differing dates for NMR analysis, the remainder being returned to the ampoule, resealed followed by additional aging. A large excess of the saturated salt solution was used in the sealed ampoules to assure that unlabeled oxygen from water in the ambient air did not contribute significantly. The details of the hydrolysis are given in Table 1. The saturated salt K_2SO_4/H_2O solutions are known to produce a relative humidity (RH) that varies little for the temperature range investigated, changing from 96.4% at 338 K to 92.4% at 398 K [26]. No corrections for this minor variation in RH with temperature were applied to the analysis of the hydrolysis products.

The solution ^{17}O NMR spectra were obtained at 338 K using a Bruker Avance 600 spectrometer at a resonance frequency of 81.39 MHz using a 5 mm broadband NMR probe. For all experiments, a standard single pulse Bloch decay pulse sequence with composite pulse ^{1}H decoupling, 128 K scan averages, a 8 μs $\pi/2$ pulse, and a 500 ms recycle delay were employed. The ^{17}O NMR chemical shifts were referenced to the secondary standard of neat, natural abundance $H_2^{17}O$ ($\delta = 0.0$ ppm) at room temperature. For all the experiments described here 25–30 mg (weight prior to aging, see Table 1) of the hydrolyzed nylon 6,6 polymer were dissolved in 750 μl of 2,2,2 trifluoroethanol (TFE). Deconvolutions of the NMR spectra were obtained using the XEDPLOT [27] software (Bruker Biospin), with the spectral intensity of the TFE resonance being used as an internal ^{17}O concentration reference, based on the natural abundance (0.037%) ^{17}O signal of TFE.

3. Results and discussion

3.1. Identification and quantification of ^{17}O-labeled species

The solution ^{17}O NMR spectra of nylon 6,6 hydrolyzed at 398 K for 6 days and 20 days in a 92.4% RH environment (containing 28.0% ^{17}O-enriched H_2O) are shown in Fig. 1(a) and (b). Very similar ^{17}O NMR spectra were obtained for the nylon 6,6 samples aged at the different temperatures (see Table 1). In Fig. 1, several distinct ^{17}O NMR resonances are observed for the hydrolyzed nylon samples. The dominant ^{17}O NMR resonance ($\delta = -14.2$ through -14.7 ppm) is assigned to H_2O that was adsorbed on the nylon material prior to dissolving the material in TFE. The ^{17}O NMR chemical shift of undiluted or neat water at room temperature is $\delta = 0.0$ ppm, but hydrogen bonding has been shown to result in major perturbations of the ^{17}O chemical shift in alcohols and ketones, including the solvent induced variations of the water resonance [20,28–30]. The assignment of the water resonance in TFE was accomplished by the addition of ^{17}O-labeled water to a sample and observing the resulting increase in signal intensity for this resonance. For the temperature range investigated between 0.75 and 2 mmol of water per gram nylon were observed, where 1.0 mmol of water per gram nylon corresponds to 1 water for approximately every 4.4 monomer units. For the nylon sample aged at 398 K a steady increase in water concentration with exposure time was observed, which was uniquely different from the other aging temperatures (see Table 1). This difference has presently has not been explained. The volatile nature of water results in the significant variation of the observed water concentration with aging time and temperature (see Table 1), and highlights a difficulty in using solution ^{17}O NMR to probe volatile species.

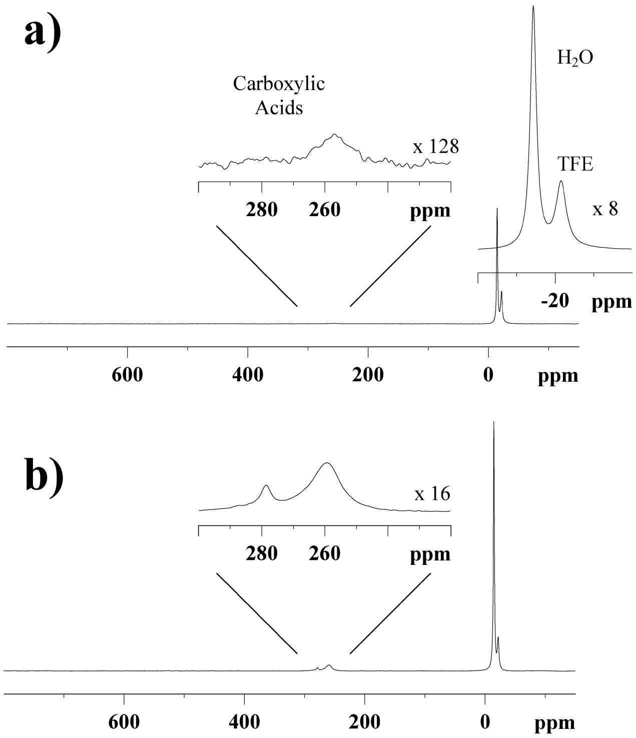


Fig. 1. The solution ^{17}O NMR spectra of nylon 6,6 dissolved in TFE following hydrolysis for (a) 6 days and (b) 20 days at 398 K.

Table 1
Aging conditions and concentrations of oxygen functionalities for the thermal hydrolysis of Nylon 6,6

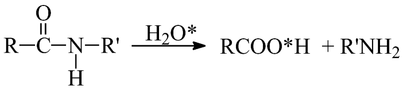
Temperature (*K*)	Time (days)	RH (%)[a]	[COOH] (mmol O/g nylon (10^{-1}))[b]	[H_2O] (mmol O/g nylon)[b]
338	63	96.4	0.38	1.18
338	84	96.4	0.16	1.37
338	105	96.4	0.50	1.04
338	126	96.4	0.31	1.40
338	147	96.4	0.51	1.71
338	170	96.4	0.38	1.45
353	14	95.8	0.16	1.19
353	28	95.8	0.14	1.14
353	42	95.8	0.22	1.29
353	100	95.8	0.80	1.18
353	112	95.8	0.83	1.69
353	126	95.8	0.84	1.53
353	140	95.8	0.97	1.25
353	156	95.8	0.99	1.06
353	170	95.8	1.01	1.40
368	21	94.9	0.66	1.52
368	48	94.9	1.20	1.97
368	64	94.9	1.70	1.44
368	86	94.9	2.09	1.28
373	15	94.5	0.59	0.74
373	28	94.5	2.78	0.45
373	42	94.5	3.80	1.56
373	82	94.5	4.93	1.49
373	124	94.5	6.01	1.43
373	240	94.5	10.4	1.74
383	8	93.7	0.83	1.21
383	15	93.7	1.06	1.66
383	21	93.7	1.59	1.00
383	28	93.7	4.53	1.02
383	42	93.7	7.40	1.60
383	82	93.7	7.80	1.28
398	3	92.4	0.57	1.56
398	6	92.4	0.71	1.30
398	9	92.4	1.59	2.44
398	13	92.4	2.40	3.97
398	16	92.4	2.31	3.26
398	20	92.4	4.28	2.59
398	23	92.4	4.44	6.69
398	27	92.4	5.26	5.66
398	40	92.4	7.00	6.25

[a] RH = relative humidity of saturated potassium sulfate solution [26].

[b] Concentration = mmol oxygen per gram unaged nylon based on the 28.0% ^{17}O isotopic enrichment of $H_2^{17}O$.

In Fig. 1, the ^{17}O NMR resonance for the natural abundance oxygen in the TFE solvent ($\delta = -21.6$ ppm) is observed just upfield of the water resonance, and is clearly seen in the spectral expansion (×8) of this region. The relative area of the ^{17}O resonance for the TFE solvent provides an excellent internal concentration standard since the solvent and sample concentration along with the natural abundance of ^{17}O (0.037%) is known. The concentrations of all other ^{17}O-containing species observed were normalized to this internal ^{17}O TFE concentration (see Table 1).

The other major ^{17}O-containing species observed are carboxylic acids which have been assigned to the multiple resonances between $\delta = +258$ and $+280$ ppm [21]. The two oxygen environments in carboxylic acids are equivalent on the timescale of the ^{17}O NMR experiment due to rapid proton exchange, and exhibit only a single ^{17}O resonance [31]. The carboxylic acid concentrations increase dramatically with higher temperatures and longer exposure times (see Fig. 1 and Table 1). The multiple acid environments observed most likely reflect different chain lengths or different nearby functionalities. Carboxylic acids are the predicted ^{17}O-containing degradation products if in the presence of water the hydrolysis of the amide bond is the dominant degradation pathway.



$$R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-R' \xrightarrow{H_2O^*} RCOO^*H + R'NH_2 \quad (1)$$

In general, there are no volatile species produced as a result of this amide bond cleavage (Eq. (1)), but secondary reactions are expected to result in CO_2, NH_3 and H_2O production [3]. During the hydrolysis reaction, one oxygen in the resulting carboxylic acid is originally derived from the ^{17}O-labeled H_2O. The solution ^{17}O NMR spectrum reveals only a single resonance for carboxylic acids due to rapid averaging of the oxygen environments. We have noted a slow oxygen exchange between the excess ^{17}O-labeled water in the high RH atmosphere and existing carboxylic acids, which can produce a further increase in the extent of ^{17}O isotope incorporation. Due to the possibility of this increased ^{17}O incorporation from slow oxygen exchange, it is impossible to accurately determine the corresponding carboxylic acid concentration based on the ^{17}O NMR experiments. Assuming a factor of two (2 oxygen per acid, or complete ^{17}O equilibration due to slow oxygen exchange), the lower concentration limit of the acid species produced during degradation can be estimated. In general, the concentration of oxygen species per gram nylon, instead of the concentration of the individual molecular species will be reported (Table 1). Inspection of the measured acid oxygen concentrations (see Table 1, especially the 338 K samples) allows an estimate of the error in quantification of the acid oxygen concentration to be about $\pm 2 \times 10^{-2}$ mmol (20 μmol) oxygen per gram nylon, which also represents the minimum carboxylic acid oxygen concentration observable for the sample size and level of ^{17}O enrichment employed.

It has been argued that the ^{17}O-labeled carboxylic acids that are observed in the ^{17}O NMR experiments are simply preexisting end group carboxylic acids from the unaged nylon 6,6 that have exchanged with the ^{17}O-enriched water in the high RH atmosphere. Using this argument the concentration of labeled carboxylic acids observed (see Table 1) would require a very small average MW (i.e. a high concentration of acid end groups) that is below a few thousand for the unaged nylon 6,6. The large MW of the unaged nylon therefore implies that the observed ^{17}O-labeled carboxylic acids are indeed the result of hydrolytic degradation.

Occasionally, extremely weak resonances between $\delta \sim +480$ and $+600$ ppm are observed for the hydrolyzed nylon samples, and are assigned to the oxygen in aldehyde or ketone degradation species. For example, the predicted formation of cyclopentanone through a cyclization step involving reactions of end group carboxylic acid groups would produce a ^{17}O NMR resonance between $\delta = +543$ and $+545$ ppm [32]. The very low signal intensity of these carbonyl species, along with the inconsistent observation of signal between samples, prevented a quantification of these degradation species, and therefore are not to be included in Table 1.

The lack of ^{17}O NMR signal corresponding to specific molecular species also provides additional details into possible degradation mechanisms. For example, a resonance between $\delta = +350$ and $+300$ ppm would be observed in the ^{17}O NMR spectra of amides. The lack of any observable amide formation shows that the reverse of Eq. (1) is not readily occurring. The generation of various lactams in low concentration has also been noted during the pyrolysis of nylon 6,6 [33]. These lactam species would give rise to a ^{17}O NMR resonance between $\delta = +320$ and $+336$ ppm [31], but were not observed experimentally. In the presence of water, lactams species would readily decompose to form carboxylic acids. It should be noted that volatile oxygen-containing species (such as CO_2) that are released to the head gas would not be observed in these ^{17}O NMR experiments. On the other hand, volatile species that are readily water-soluble should be observable due to the high amount of adsorbed water present in the aged nylon samples analyzed (see Table 1).

3.2. Temperature variation of carboxylic acid formation

The variation of the acid concentration with temperature and aging time is shown in Fig. 2 (also see Table 1). In general, there was an increase in the concentration of ^{17}O-labeled carboxylic acid oxygen produced with both increased exposure times and increased temperatures. The rate of acid production becomes faster with increasing temperature. A leveling-off or reduction in the overall acid oxygen concentrations was observed for the higher temperatures at longer exposure times (for example, see the 383 K data in Fig. 2). The reduction in the rate of ^{17}O-labeled acid oxygen production in the hydrolyzed nylon at longer aging times may result from secondary reactions, but these reactions were not extensively analyzed in the present study.

The initial rate of ^{17}O-labeled acid oxygen production as

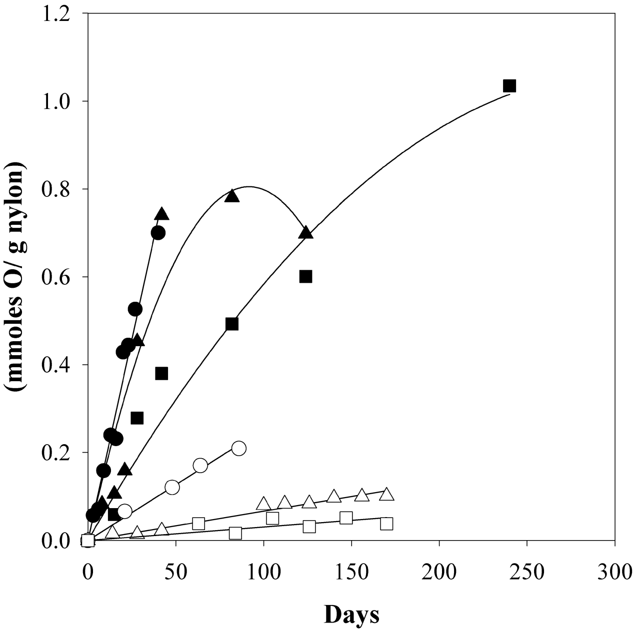


Fig. 2. The variation of the carboxylic acid oxygen concentration in hydrolytically aged nylon 6,6 as a function of exposure time and aging temperature: (□) 338 K, (△) 353 K, (○) 368 K, (■) 373 K, (▲) 383 K and (●) 398 K. Lines are for visual guide only.

a function of temperature can be used to estimate the energy of activation for hydrolysis. The Arrhenius fit of the rate of carboxylic acid production with inverse temperature is shown in Fig. 3, which yields an activation energy (E_a) of approximately +87 ± 1 kJ/mol. This value is very similar to the +81.85 kJ/mol previously reported for the degradation of nylon 6,6 fibers [34], and the +81 to +87 kJ/mol reported for the polyamide PA-11 in a pH 7 water environment [12].

The effect of diffusion-controlled hydrolysis in nylon 6,6 has not been investigated in detail. Based on a series of studies for polyamide 11 materials [10,13], the critical sample thickness was found to be ~3–8 cm between 373 and 413 K, suggesting that for the nylon fibers (~10–50 μm) investigated in this study diffusion control of the hydrolysis reaction can be neglected.

4. Conclusions

Solution ^{17}O NMR spectroscopy has been used to study the thermal hydrolysis of nylon 6,6. These NMR studies confirm that under high humidity conditions the predominant degradation mechanism of nylon 6,6 is the hydrolysis of the amide bond. No significant concentrations of other oxygen-containing degradation species were observed during the hydrolytic aging between 338 and 398 K. Reactions involving the significant production of ^{17}O-labeled cyclopentanone or amide degradation species were not observed in the ^{17}O NMR experiments. The variation of the carboxylic acid concentration as a function of temperature allowed the activation energy of +87 ± 1 kJ/mol to be determined. Further ^{17}O NMR investigations on the influence of oxygen atmosphere on the rate of hydrolysis in nylon 6,6 are presently being pursued and will be reported elsewhere.

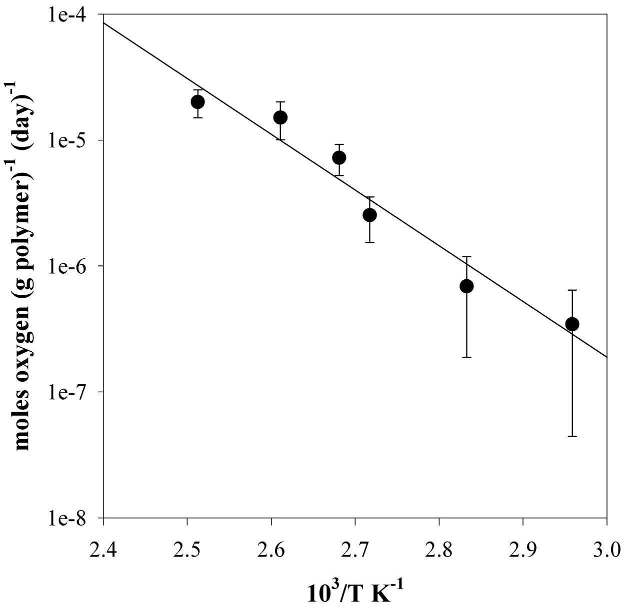


Fig. 3. Arrhenius plot of the initial rate of carboxylic acid oxygen production in nylon 6,6 for the temperature range 338–398 K.

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