



Polyamide hydrolysis accelerated by small weak organic acids



Samuel Hocker^a, Anne K. Rhudy^b, Gregory Ginsburg^b, David E. Kranbuehl^{b,*,1}

^a Department of Applied Science, The College of William and Mary, 540 Landrum Dr, Williamsburg, VA, USA

^b Department of Chemistry, The College of William and Mary, 540 Landrum Dr, Williamsburg, VA, USA

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ABSTRACT

It is well known that acidity, pH, of a solution accelerates the hydrolysis of soluble amides. Here we describe the unexpected result that weak small organic acids at low concentrations hydrolyze a polyamide at rates approximately twice that of a water HCl solution of the same pH. The effect of three small organic acids in dilute solutions, acetic, propanoic, and butanoic was studied. It is observed that the effect on the hydrolysis rate increases as the organic acid gets weaker. Butanoic, the weakest acid, has the strongest effect on increasing the hydrolysis rate. Measurements on the concentration of these acids in the polyamide reveal that there is a selective desire for these weak organic acids to diffuse into the polyamide. The concentration of these acids in the polyamide is found to be several multiples of the concentration in the water environment. And the acid concentration is highest for butanoic. The hydrolysis rate is shown to be governed by solubility, not pH of the water environment. The longer hydrocarbon tail on the carboxylic group increases its compatibility with the polyamide's monomer structure. Results are reported on the hydrolysis of polyamide-11 polymerized from aminoundecanoic acid, both neat and a commercial plasticized composition, placed in water at 100 °C and 120 °C under anaerobic conditions in high pressure glass tubes.

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1. Introduction

It is well known that acidity, pH, of a solution accelerates the hydrolysis of soluble amides. Here we describe the unexpected result that weak small organic acid at low concentrations hydrolyze a polyamide at rates approximately twice that of a water HCl solution of the same pH. The effect of three small organic acids in dilute solutions, acetic, propanoic, and butanoic was studied. It is observed that the effect on the hydrolysis rate increases as the organic acid gets weaker. Butanoic, the weakest acid, has the strongest effect on increasing the hydrolysis rate. Measurements on the concentration of these acids in the polyamide reveal that there is a selective desire for these weak organic acids to diffuse into a polyamide. The concentration of these acids in the polyamide is found to be several multiples of the concentration in the water environment. And the acid concentration is highest for butanoic.

This result is important not only because it differs from the widely expected dependence on pH but because polyamides (nylons) are frequently used in everyday life and are the preferred polymer in critical applications involving hydrocarbons. Polyamide-11, because of the lower number of amide bonds for a given chain length, is widely used throughout the world as a pressure sheath in flexible pipes to transport crude oil from the ocean floor to platforms. It is also used as a liner in steel pipes for crude transport over land. When polyamide-11 is used as the barrier in pipes for transporting crude, which is a mixture of hydrocarbons and water, over time hydrolytic degradation of polyamide-11 occurs. This can result in low molecular weights where polyamide-11 loses its ductility and becomes brittle. This is the so called ductile–brittle transition [1,2]. Knowing that the molecular weight at a given time is above the ductile–brittle transition onset molecular weight is the primary factor for continued safe use. Understanding the factors governing amide hydrolysis kinetics is therefore not only of fundamental scientific interest but essential in understanding polyamide's useful life.

The kinetics of polyamide degradation in water has been extensively studied [3–13]. The existence of an equilibrium molecular weight, which occurs when the rates of hydrolysis and re-polymerization become equal, was established for varied temperatures and initial molecular weights [3–5]. Studies have examined

* Corresponding author.

E-mail addresses: jshock@email.wm.edu (S. Hocker), dekran@wm.edu, dekran@gmail.com (D.E. Kranbuehl).

URL: http://www.wm.edu/as/chemistry/people/emeritus_faculty/kranbuehl_d.php

¹ Romão et al. report measurements of corrected inherent viscosity, and to interpret their results we applied our Mark–Houwink parameters for polyamide-11.

the hydrolytic degradation of both neat and plasticized PA-11 in environments of water [3–11], salt water [10], oilfield water [6], crude oil [6,10], and in acidic [5,12,13] conditions.

Jacques et al. and Meyer et al. have both shown that in the absence of oxygen, polyamide-11 reaches an equilibrium molecular weight when aged in deionized water [3,4]. Acidic conditions have been shown to accelerate amide hydrolysis [5,6,11,12,14]. The chemical effects that acids have on polyamide hydrolysis are amine scavenging and acid catalysis [5,15–19]. Merdas et al. showed that the average equilibrium molecular weight (\bar{M}_{me}) of aged polyamide-11 is lowered in carbonic acid, pH 4, by approximately 1 kDa at 130 °C and 3 kDa at 160 °C due to CO₂ solubility in the polymer [5]. They also propose a model to predict the equilibrium molecular weight for polyamide-11 aged in an acidic aqueous environment. Their model requires the acid concentration within the polyamide-11 matrix to be known. Merdas et al. suggest that for weak acids there is no catalytic effect and that weak acids could effect polyamide-11 hydrolysis by shifting the equilibrium towards lower values of \bar{M}_{me} [5]. Chaupart et al. reported a strong pH acid effect on polyamide-11 hydrolysis at low pH's of 4, 2, and 0 [13]. But the presence of oxygen was uncontrolled and an equilibrium was not observed. The absence of an equilibrium is now the expected result when oxidation and hydrolysis are both degrading the polyamide chain. Naphthenic carboxylic acids in crude oil are also known to accelerate the degradation process beyond the aging in pH 7 water. Naphthenic acids have been shown to degrade polyamides primarily on the surface [20].

Recently, Romão et al. aged polyamide-11 in oilfield water, with a pH of 5.5 [6]. They report a very large equilibrium molecular weight decrease (10 kDa¹) compared with deionized water. Such a significant decrease of the equilibrium molecular weight remains unexplained by the oilfield water pH of 5.5. Here we propose that this result is related to other molecular species in the oilfield water, particularly small hydrocarbon acids such as acetic acid, which is found in many oilfields.

The work herein reveals the importance of understanding the molecular species present during hydrolytic degradation conditions. We report on the significant increase in the rate of degradation caused by small organic acids and discuss the molecular basis for the unexpected large effect of weak organic small acids, acetic, propanoic, and butanoic.

Here it is shown that the smaller and much weaker organic acids significantly accelerate degradation process even more than HCl water at similar pH conditions. This effect occurs at the very low concentrations of small organic acids often found in crude oil reservoirs. Characterization of this surprising effect of weak, small organic acids on the rate of degradation is one objective of this work. Determining the effect of the organic acid's structure and concentration is another. Most important is development of a fundamental understanding of why the rate of degradation in uncorrelated with the small organic acids acidity and is so strong given the very low acidity of small organic acids. This report focuses on the effect of three low molecular weight organic weak acids (acetic, propanoic, and butanoic) on accelerating the aging of polyamide-11 at 100 °C and 120 °C, at a constant molarity.

2. Materials and methods

2.1. Making polyamide-11 coupons

Polyamide-11 was made in our laboratory by heating the monomer, 11-aminoundecanoic acid, purchased from Sigma–Aldrich, at 240 °C for 3 h. The polymer material was then pressed into the form of a film, 15 × 7 × 0.25 cm. The film was punched into 1 cm diameter cylinder coupons for aging.

Commercially polymerized polyamide-11 Besno P40TL made by Arkema was supplied by National Oilwell VARCO of Denmark. The commercial PA-11 has n-butyl benzene sulfonamide (BBSA) at 12 wt% to function as a plasticizer. The function of the plasticizer is to disrupt hydrogen bonding in the amorphous region of the polymer matrix [21]. Coupons having a cylindrical shape with 1 cm diameter and 1 cm thickness were punched from this extruded polyamide-11.

2.2. Aging conditions

The coupons were immersed in deionized water and controlled acidic solutions over a period of months at controlled constant temperatures of 100 °C and 120 °C to accelerate aging. Ace #40 high pressure rated glass tubes with teflon plugs were used as the containment vessels. Dissolved oxygen was removed, to avoid oxidation effects, by sparging the aging solution with argon in the containment vessel to keep the oxygen level below 50 ppb.

One set of aging solutions was made using three small weak organic acids: acetic, propanoic, and butanoic. Each acid was mixed with deionized water at a concentration of 1.05×10^{-2} M. Deionized water was the control aging solution. Previous work has characterized the molecular weight degradation behavior of polyamide-11 aged in deionized water for a range of temperatures [3,5–11]. Laboratory made PA-11 coupons were aged in these 1.05×10^{-2} M small organic acid solutions at 100 °C and 120 °C.

A second set of aging solutions was made to create a range of pH values and conditions to explore the effect of H⁺ ions at pH conditions similar to that of the three weak organic acids. A hydrochloric acid solution with a pH of 2.9 was prepared by diluting HCl into deionized water. Acetic acid was diluted into deionized water to 6.29×10^{-2} M and a pH of 2.9. A carbonic acid solution, having a pH of 4.2, was prepared by bubbling deionized water with carbon dioxide for 15 min at a flow rate of 400 mL/min. Finally, a buffer solution was used to control the ratio of protonated and deprotonated acetic acid during aging. Since a buffered solution has a known pH, this ratio is easily calculated using the Henderson–Hasselbach relationship, equation (1) [22,23]. In the buffered system, significantly more acetic acid exists in the de-protonated form, compared to a normal system. Sørensen's phosphate buffer was used, which consists of monobasic and dibasic sodium hydrogen phosphate. The buffer was prepared at a 0.3 M concentration and used to create an acetic acid 6.29×10^{-2} M solution with a buffered pH of 6.2. The punched commercial extruded PA-11 coupons were immersed in the environments at 100 °C.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (1)$$

2.3. Measuring mass average molecular weight, \bar{M}_m , and crystalline content

Multiple in-line SEC columns (HFIP-LG, HFIP-805, and HFIP-803 from Shodex with packing beads composed of a polystyrene-divinyl benzene copolymer) with a Wyatt miniDAWN light scattering and Wyatt Optilab 803 dynamic refractive index detector were used to measure the molecular weight. The miniDAWN has a laser wavelength of $\lambda = 690$ nm and three detection angles $\theta = 45^\circ$, 90° , and 135° . A dn/dc of 0.235 determined the concentration of the polyamide-11 at each fraction.

The solvent used to dissolve the polymer samples was 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) doped with 0.05 M Potassium Tri-Fluoroacetate (KTFA) salt to remove nylon agglomerations [24]. The solvent was degassed in the pump reservoir via constant

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