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A Study of the Aging of Polyamide-11 Based on Molecular Weight Measurements

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A STUDY OF THE AGING OF POLYAMIDE-11 BASED ON MOLECULAR WEIGHT MEASUREMENTS

A Thesis
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In Partial Fulfilment
Of the Requirements for the Degree of
Master of Arts

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by
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2000

APPROVAL SHEET

This thesis is submitted in partial fulfilment of

the requirements for the degree of

Master of Arts

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Approved, August 2000

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Abstract

The focus of this study is to characterize the degradation of polyamide-11 in accelerated aging environments by using molecular weight measurement methods, to understand the molecular mechanism and kinetics of polyamide-11's degradation, and thereby to develop a model to predict the usable life of polyamide-11 pipe in the given environment.

High Pressure Size Exclusion Chromatography - Light Scattering system (HPSEC-LS) with the mobile phase of 1,1,1,3,3,3-Hexafluoro-isopropanol (HFIP) can accurately measure the absolute value of weight average molecular weight of polyamide-11 at room temperature. Thus this system provides a convenient and sensitive means to monitor the aging of polyamide-11. Neither universal calibration Size Exclusion Chromatography (SEC) nor conventional SEC method can provide the same capability.

A model for the degradation kinetics of polyamide-11 has been developed based on the hypothesis that the degradation process for polyamide-11 approaches an equilibrium between hydrolysis-chain scission and polymerization-recombination. The model fits the weight average molecular weight data for aging of polyamide-11 in pure water, and the temperature dependence of molecular weight of aging polyamide-11 at equilibrium and reaction rate related parameters are studied. Future work will concentrate on the mechanism and kinetics of aging of polyamide-11 in the present of acid and alcohol, and the role of plasticizer in the aging process.

A STUDY OF THE AGING OF POLYAMIDE-11
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Chapter 1: Introduction

The focus of this study is to characterize the degradation of polyamide-11 in accelerated aging environments by using molecular weight measurement methods, to understand the molecular mechanism and kinetics of polyamide-11's degradation, and thereby to develop a model to predict the usable life of polyamide-11 pipe in the given environment.

Polyamide-11, poly(imino-1-oxoundecamethylene), is made by the step condensation polymerization of 11-aminoundecanoic acid at around 220°C.[1] Polyamide-11 has good flexibility, high strength, good chemical resistance and the ability to withstand a high load. Compared with Nylon-6 and Nylon-66, polyamide-11 absorbs much less water because it has a lower ratio of hydrophilic polar amide groups than the other two.[2] These properties make polyamide-11 a good choice for use in oil pipes, typically as the inner barrier layers.[3] These polyamide-11 lined oil pipes are located throughout the world, primarily in the North Sea, the Gulf of Mexico and off the coast of Australia.

As we can imagine, the use environment of polyamide-11 pipes is very harsh. For example, on the outside the pipes in the North Sea face extremely unpredictable weather, high pressure since water depth could be more than 1000m, seawater temperature of around 3°C at depths below 10m. On the inside, the pipes are exposed to high internal fluid temperature from 50°C to 90°C, and high internal pressures up to 50 bar.[3] In such environments, polyamide-11 degrades with time, leading to a decrease of the molecular weight, failure of the mechanical properties, and finally breaking or rupturing of the pipes.

In order to avoid this kind of possible environmental disaster while optimizing the usable life of Nylon pipe, it is necessary to understand the degradation mechanism of polyamide-11. Models are needed to understand and predict the life span based on characterization of the polymer's degradation rate in different use environments. In situ methods[4] are needed to monitor the aging process while the pipe is in use in order to update the aging model's predictions in the changing environment.

Based on the use environment of polyamide-11 pipe, different simulated aging environments have been set up in our laboratory, for example, different water concentrations in oil, different pH's, either inorganic or organic acid, different additives such as methanol and ethylene glycol which prevent freezing, and different oxygen concentrations. Most important, temperature baths from 60°C to 130°C are used to study the temperature dependence of aging rate of polyamide-11 for these environments. Monitoring the aging of polyamide-11 has been performed, using mechanical tensile tests, molecular weight measurement and frequency dependent electromagnetic sensing system (FDEMS). The results from different methods are being correlated.

Earlier work in our laboratory produced several conclusions. First, the major chemical degradation mechanism causing the aging of polyamide-11 in an oil-water environment was hydrolysis, even when as little as 1% water is present.[7, 8] Second, the mechanical tensile tests are a poor method for monitoring rate of aging and useable life of polyamide-11 as these properties change little until the onset of failure, usually during the last 10% or so of the useable life.[5,6,8] Third, molecular weight measurements are ideal methods for monitoring life remaining and performance properties of polyamide-11.[7,8] Fourth, FDEMS can be used as an in-situ method to monitor the aging process of polyamide-11.[5]

Therefore, this study focuses on the hydrolysis degradation of polyamide-11 and developing a model to predict the life span based on characterization of polyamide-11 by molecular weight measurements. Since commercial polyamide-11 typically has plasticizer added, it is important to avoid unexpected effects from plasticizer. Therefore different molecular weight (Mw from 10k to 80k) unplasticized polyamide-11 samples have been made from monomer by self-step condensation reaction in the lab. For this study on the hydrolysis of polyamide-11, pure deionized water aging environments under argon gas for protection from oxygen have been used. Different initial molecular weight polymer sample bars have been put into each aging environment in the 70°C, 80°C, 90°C, 105°C, and 120°C temperature bath. Then, characterization of degradation of the polyamide-11 samples is done using High Pressure Size Exclusion Chromatography – Light Scattering system(HPSEC-LS), and Size Exclusion Chromatography - Viscotek system (SEC-Viscotek) in our lab.

It is well known that the amount of longer chains determines and controls the elasticity of polymer.[9] Thus we have suggested that molecular weight is the principal parameter governing changes in the performance properties of Polyamide-11 in flexible pipes.[7] Further we believe that the molecular weight distribution is particularly informative and accurate for monitoring changes in mechanical performance properties which affect use and lifetime.[10] In our lab, a size exclusion chromatography system with a laser light scattering molecular weight detector and a refractive index concentration detector has been set up. This system has the ability to make absolute measurement of the concentration of each molecular weight chain length for each polymer chain as it elutes past the detection system.[11] The HPSEC-LS system provides us a convenient, room temperature, accurate and sensitive means to monitor changes in molecular weight and the molecular weight distribution. This method is the principle means used to monitor aging, life remaining and the performance properties of polyamide-11.

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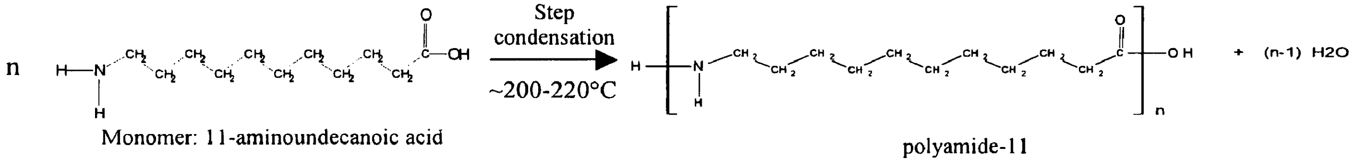
Chapter 2: Background

I. Polyamide-11, Rilsan

Polyamide-11 or poly(ω-aminoundecanoic acid) was first prepared by Carothers in 1935. It was first manufactured commercially in France in 1955, where the polymer is known as Rilsan.[1] The monomer is prepared by oxidizing castor oil to undecylenic acid. The latter is then treated with HBr and ammonia to form ω-aminoundecanoic acid. High molecular weight polyamide-11 is prepared in about 3 hours by melt polymerization of the amino acid at 215°C under nitrogen. The water formed is continuously removed. The final polymer can be extruded into pellets under inert gas to prevent oxidation.[1] The reaction is:



II. Properties of polyamide-11

Typical properties[2] of polyamide-11 are given in the Table 2.1.

Table 2.1 Properties of commercial polyamide-11.

Property	Polyamide-11
Specific gravity	1.04
Glass transition temperature T_g, °C	57
Melting temperature T_m, °C	194
Tensile strength, MPa	54
Elongation at break, %	200-330
Modulus, MPa	1730
Water absorption, wt%	
24 h	0.3
Equilibrium at 50% rh	0.8
Saturation	1.9
Dielectric constant, MHz	4.0
Dissipation factor, MHz	0.03
Specific heat, J/(g.K)	1.26

III. Degradation of Polyamide-11 by Hydrolysis

Polyamide, which is synthesized by condensation reactions, is particularly susceptible to degradation by hydrolysis. Polyamide-11 degrades in the presence of strong bases, acids, and oxidants. When water is present, the molecular mechanism of degradation is a two step process: first diffusion, which means water penetrates into the polymer; then hydrolysis, which means chain scission occurs at the C-N bonds along the polymer chain backbone.[3,4,5] This step can be acid catalyzed or base catalysed. The hydrolysis usually takes place in the amorphous regions of the nylon.

In acid-catalyzed hydrolysis, cleavage of the carbon-nitrogen bond is initiated by protonation of the carbonyl oxygen atom. Second, water attacks the carbonyl carbon atom, resulting in the formation of an oxonium ion. Third, deprotonation of the oxonium ion yields the neutral diol form of the intermediate. Fourth, protonation of the amino nitrogen results in an ammonium ion. Fifth, the ammonium ion dissociates to form an amine. Sixth, the acid is deprotonated to yield the carboxylic acid.[6] The scheme is shown in Figure 2.1.

Conversely, strong base catalysed hydrolysis is initiated by hydroxide ion attack of the carbonyl carbon atom, with a similar sequence of events.

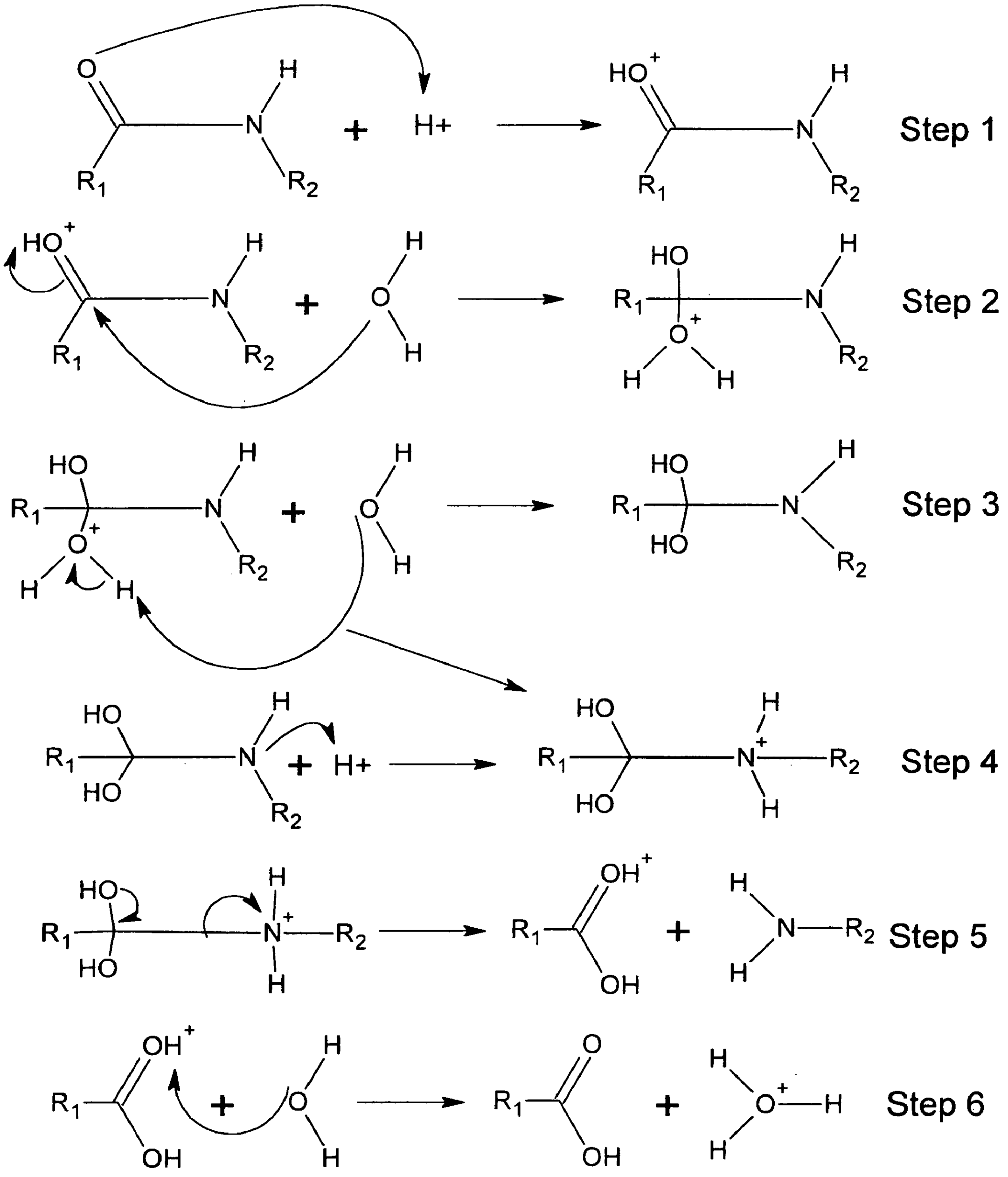


Figure 2.1: A mechanism for acid-catalyzed hydrolysis of polyamide-11

IV. Solid State Polymerization of Polyamide-11

Postcondensation of polyamides in the solid state has been known for many years and the method is used in industry to produce high molecular weight materials.[7] Usually, medium to low molecular weight semi-crystalline prepolymers of polyamides can be subjected to further polymerization at temperatures between the melting point and the glass transition temperature of the polymer. This phenomenon is commonly known as solid-state polymerization (SSP).

A comprehensive effort to understand the mechanism and kinetics of the solid state polymerization started over three decades ago, but the attempts to interpret experimental data were quite dispersed and semi-empirical in nature.[8] Generally, it is agreed that the polymerization in the solid state does not follow the melt polymerization kinetics.[7,9,10] The reaction seems to be slowed by diffusion. The limiting process might be the diffusion of the condensate(water) out of the particle or the diffusion of the reactive end groups in the solid.[11]

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Chapter 3: The Techniques and Methods of Molecular Weight Measurement

The physicochemical properties that give polyamide-11 excellent strength, toughness and solvent resistance also complicate the analysis of its molecular weight and molecular weight distribution via size exclusion chromatography (SEC).[1] The choice of suitable solvents for the mobile phase in the SEC of polyamide-11 is limited. 1,1,1,3,3,3-Hexafluoro-isopropanol is among the few room temperature solvents for polyamide. Former work by Costa *et al.*[2] suggests that when HFIP has been used as a SEC solvent, it required the addition of sodium trifluoroacetate (NaTFA) to obtain a unimodal Gaussian shaped peak for nylon-66. Without this salt, the chromatogram was bimodal, which was attributed by Drott[3] to the poly-electrolyte effect. Polyeletrolytes are macromolecules which, when dissolved in a suitable polar solvent, spontaneously acquire a large number of electric charges. The behavior or the physical properties of solutions containing electrically charged chains can differ considerably from what is observed for the more conventional solutions. This phenomon occurs in low pKa solutions where protonation of the amide nitrogen yields polymric ammonium ions, causing intramolecular repulsion and expansion of the chain.[4]

The objective of this chapter is to present the techniques and methods of molecular weight measurement used in our laboratory. HPSEC-LS system with the mobile phase of HFIP is our principle means to measure the absolute molecular weight of polyamide-11. A second HPSEC-Viscotek system with the mobile phase of HFIP plus NaTFA has been developed to study the polyamide-11's behavior when we use the universal calibration. Thus we are able to compare the salt effect on the conventional calibration SEC for the two systems, one in the mobile phase of HFIP with NaTFA and the other in HFIP without NaTFA.

I. HPSEC-LS system

A. HPSEC-LS system basic principles

Light scattering is one of the few absolute methods available for the determination of molecular mass and structure and is certainly applicable over the broadest range of molecular weights of any methods.[5]

High Pressure Size Exclusion Chromatography (HPSEC) has the ability to analyse the distribution of broadly polydisperse samples as well as to obtain details of branching and molecular conformations. Thus, by combining light scattering and HPSEC, the weight, number and z-average values for both mass and size may be obtained for most samples, as well as the ability to calculate both differential and cumulative distributions of molecular weights and mean square radii.[5]

There are two basic principles of light scattering. One is that the amount of light scattered is directly proportional to the product of the polymer molar mass and concentration. The other is that the angular variation of the scattered light is directly related to the radius of the molecule.[6]

The basic Zimm[7] formalism of the Rayleigh-Debye-Gans light scattering model for dilute polymer solutions is:

$$\frac{Kc}{R(\theta)}(1+\cos^2\theta)=\frac{1}{MwP(\theta)}+2A_2c \qquad (3.1)$$

where

$$K=4\pi^2\left(\frac{dn}{dc}\right)^2 n_0^2 N_A^{-1}\lambda_0^{-4} \qquad (3.2)$$

$$\frac{1}{p(\theta)}=1+\frac{16\pi^2}{3\lambda^2}\left\langle r_g^2\right\rangle\sin^2\left[\frac{\theta}{2}\right]+\ldots \qquad (3.3)$$

n_0 is the refractive index of the solvent

N_A is Avogadro's number

λ_0 is the vacuum wavelength of the incident light

dn/dc is the refractive index increment

c is the concentration of the solute molecules(g/ml)

R(θ) is the Rayleigh ratio, which is related to the scattering intensity

Mw is the weight-average molar mass

A_2 is the second virial coefficient, which is a measure of solvent-solute interaction

P(θ) is the form factor or "scattering function", telling how the scattered light varies with angle. This variation is determined by $<r_g^2>$, the mean square radius.

So, by knowing the value of refractive index of the solvent, wavelength of the incident light, dn/dc of the measured polymer, an appropriate software program such as Wyatt's ASTRA program uses the above equations based on the signals collected by light scattering detector and refractometer to generate molecular weight and size parameters for each so-called eluant slice immediately following chromatographic separations. Then after integration, both the average molecular weight information and molecular weight distribution information can be obtained.

B. HPSEC-LS system set up

The HPSEC-LS system consists of the following equipment: Waters 515 HPLC pump, Jordi Gel DVB mixed bed HPLC column, Wyatt/Optilab 903 interferometric refractometer, Wyatt miniDAWN light scattering instrument (Laser wavelength=690nm) and Rheodyne 7725 manual sample injector.

The mobile phase is 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, Oakwood Products, Inc., Laboratory Use, RI=1.275) operated at a flow rate of 0.60ml/min. The columns are placed in the water bath with an temperature of 40.0°C. Injection volume is 20μl with sample concentrations of around 5.0mg/ml. Samples are dissolved in either HFIP or meta-cresol. Solvents have been distilled to remove the moisture and filtered through 2μm inline filter. The chromatograms are integrated by the software ASTRA and have good reproducibility and a stable baseline.

C. LS calibration

As an absolute method to measure the molecular weight of polymer, HPSEC-LS system does not need column calibration by using other polymers as standards. But we do need to calibrate the miniDAWN and RI detector and determine the delay volume and the normalization coefficients for the initial system set-up.

The miniDAWN calibration constant, which is the proportionality constant between the miniDAWN output voltage and the light scattering intensity, can be determined by flowing pure, filtered toluene through the flow cell.[8]

ASTRA software measures the voltages from the 90-degree detector and the laser monitor photodiodes with the laser on and with the laser off. Then the calibration constant can be computed by ASTRA. The calibration constant for our system is 1.000E-5. The calibration constant determined using toluene is valid with any solvent.

The RI detector calibration constant is the proportionality constant between the difference in refractive index and the change in the RI detector voltage. When performing RI detector calibration, we prepared calibration standard solutions with known concentrations (c) and known dn/dc (NaCl in water), and computed $\Delta n = c*(dn/dc)$ for each standard solution. Then each standard is passed through the RI detector and the RI detector voltage (ΔV) is recorded. After plotting Δn vs. ΔV, the slope is the RI calibration constant, $RI_{cc} = d(\Delta n)/d(\Delta V)$.[9] The Wyatt Company performed the RI constant for our system. The value is 1.0664E-4 $volt^{-1}$.

Because the photodiode detector at the different angle senses a different scattering volume and each photodiode has a slightly different sensitivity, they need to be normalized relative to the 90-degree detector using an isotropic scatterer. We use narrow distribution PMMA standard (Mp =10.0kg/mol, Mw/Mn=1.04) to perform the normalization. (Mp is the molar mass at the peak). The ASTRA software measured the scattering voltages from the three different scattering angles in our system, and computed the normalization coefficient for each detector. For our system, table 3.1 shows the normalization coefficients for each scattering angle:

Table 3.1: Normalization Coefficients for Light Scattering Detectors

Detector Number	Scattering Angle	Normalization Coefficients
1	38.6°	0.998
2	90.0°	1.000
3	141.4°	1.020

After finishing the normalization, the alignment process also needs to be performed in order to determine the delay volume between the light scattering and the RI detector. We used a monodisperse PMMA standard (Mp=69.0kg/mol, Mw/Mn=1.03) and ASTRA calculated the delay between miniDAWN and refractometer to be 0.190ml.

In summary, table 3.2 below shows the fundamental instrumental parameters for our system.

Table 3.2: Instrumental Parameters for HPSEC-LS system

MiniDAWN Calibration Constant	1.0000E-5
RI Calibration Constant (volt^{-1})	1.0664E-4
Delay volume(ml)	0.190

D. Accuracy checking

A few narrow dispersed PMMA standards (PMMA1-PMMA9) were purchased from Polymer Laboratories Ltd, UK for the purpose of calibration and accuracy checking. The Mp of the standards ranges from 2.4 kg/mol to 910 kg/mol. Polymer polydispersity varied from 1.03 to 1.10 as reported by the Polymer Laboratories Ltd. The Mn, Mw, Mv and Mz data measured by the company from GPC, Light Scattering and Viscometry are also supplied. In addition, several nylon-66 (nylon-66, B) and nylon-6 standards from American

Polymer Standards Co., one polyamide-66 standard sample (nylon-66, A) and one PET standard sample from Dupont Company were also used in our laboratory to check the calibration.

After setting up all the calibration constant and instrumental parameters, several PMMA standard samples and Nylon 66 standard samples were used to check the accuracy of our instrument. The value of dn/dc for PMMA in HFIP is 0.188mL/g, and the value of dn/dc for polyamide-66 in HFIP is 0.241mL/g. This type of routine check is performed at least every two months. Table 3.3 reports the results. At least three runs were performed for each samples. The errors are in 95% confidence level.

Table 3.3: Molecular weight measurement of polymer standards by HPSEC-LS

	Company Reported					**HPSEC-LS Measured**		
	GPC Mp (kg/mol)	**GPC Mn (kg/mol)**	**GPC Mw (kg/mol)**	**GPC Mw/Mn**	**LS Mw (kg/mol)**	**Mn (kg/mol)**	**Mw (kg/mol)**	**Mw/Mn**
PMMA1	2.4	2.2	2.4	1.08	NA*	2.2±0.2	2.3±0.2	1.03±0.05
PMMA2	4.9	4.5	4.9	1.10	4.9	4.5±0.2	4.6±0.2	1.03±0.02
PMMA3	6.9	6.4	6.9	1.07	6.3	6.2±0.2	6.6±0.2	1.01±0.02
PMMA4	10.0	9.3	9.6	1.04	10.3	9.7±0.4	9.8±0.2	1.01±0.02
PMMA5	22.7	21.7	22.3	1.02	NA	22.5±0.4	22.6±0.4	1.01±0.01
PMMA6	28.9	27.7	28.3	1.02	NA	29.4±0.1	29.5±0.0	1.01±0.01
PMMA7	69.0	66.1	68.0	1.03	75.8	70.3±1.9	70.9±1.4	1.01±0.02
PMMA8	212.0	200.3	209.8	1.05	NA	209.9±3.7	212.0±2.1	1.02±0.02
PMMA9	910.5	938.9	992.2	1.06	NA	866.9±6.3	869.9±6.0	1.00±0.02
Polyamdie-66, A	24.7	17.5	35.0	2.0	NA	25.6±3.3	35.1±0.5	1.39±0.19
Polyamide-66, B	31.0	20.8	46.2	2.22	NA	34.1±0.7	47.5±1.0	1.39±0.04
PET	NA	22.0	44.0	2.0	NA	37.4±1.1	44.6±1.2	1.20±0.06

*NA: Not Available

Comparing with the HPSEC-LS measured Mw and the company reported Mw for the same standards, we conclude the HPSEC-LS system has been properly set up and can accurately measure weight average molecular weight of the samples. The only exception is sample PMMA9, with a 12% deviation from the company reported value. The reason is that the miniDAWN Light Scattering system has a upper measurement limit of about a 1000kg/mol. PMMA9 has a large molecular weight (Mw=992kg/mol) which approaches the upper limit of miniDAWN, thereby it has relatively high deviation. Since for polyamide-11, the Mw is typically under 100kg/mol, this deviation at the very high molecular weight range will not affect our analysis.

E. Online dn/dc measurement

The specific refractive index increment is dn/dc. In other words, it is the change in the refractive index of a polymer solution relative to the change of the polymer concentration. Before we can perform any molecular weight measurement of polyamide-11 samples in our HPSEC-LS system, we must have the dn/dc value for polyamide-11, in our solvent of HFIP, at our wavelength of 690.0nm, at our setting temperature. Since it is not in the literature, we performed on-line dn/dc measurement in our laboratory.

First, several unplasticized polyamide-11 samples have been dissolved in HFIP with accurate measurement of the concentration. Exactly 20µl sample solution was injected into the system with the columns bypassed. ASTRA software computed an on-line dn/dc value with the setting of 100% mass recovery. The results of the on-line dn/dc measurement are listed in table 3.4.

Table3.4: online dn/dc measurement of polyamide-11

Sample Description	Dn/dc(mL/g)	LS Mw(kg/mol) (Using dn/dc=0.335)
Unplasticized polyamide-11, #060399	0.335±0.009	72.0±1.2
Unplasticized polyamide-11, #060799	0.305±0.005	77.8±1.1
Unplasticized polyamide-11, #061799	0.312±0.008	30.0±0.6
Unplasticized polyamide-11, #062899	0.306±0.005	14.6±0.7
Polyamide-11 (PA 1368 PFE)	0.326±0.003	51.5±0.5
Wellstream Nylon bars*	0.331±0.007	49.0±2.0
ω-aminoundecanoic acid ($C_{11}H_{23}NO_2$)	0.105±0.002	0.201 (Formula Molecular Weight)

*Mach. Nylon bars are commercial products. From TGA measurements, we know that they contain about 12.5% additives, so we assume 87.5% mass recovery for our dn/dc on-line measurements.

For most homopolymers, the value of dn/dc remains constant over a broad range of molecular weights. But the value of dn/dc begains to change appreciably as the molecular weight falls below about 10kg/mol. Average dn/dc values are often sufficient for the determination of weight average molecular weights of bulk samples. [5]

The results of dn/dc measurements in table 3.4 show that dn/dc decreases about 9% when weight average molecular weight drops from 72.0kg/mole to 14.6kg/mole. The sample #060799 has a smaller dn/dc, which might be caused by different thermal history. Unlike other samples, this one was quenched by liquid nitrogen to stop the polymerization.

Because of the agreement of the high molecular weight unplasticized polyamide-11(#060399) and commercial polyamide-11(Wellstream Nylon Bar and PA1368-PFE), a dn/dc value of 0.335 for polyamide-11 in HFIP was used in these studies, at the wavelength of 690nm and room temperature. We chose the average of the measured dn/dc for unplasticized polyamide-11 #060399 instead of doing the average with the other two commercial samples because for the commercial products, dn/dc measurements also depend on the TGA's measurement of weight percentage of additives, which might bring some deviation. And even if the dn/dc changes from 0.335 to 0.331, there will be less than 1.5% changes in the values of weight average molecular weight, it's within the experimental error of light scattering measurement itself.

II. Universal calibration SEC-Viscotek system

A. Principal of universal calibration

The universal calibration, introduced by H. Benoit *et al.*,[10] is based on separation of polymer by the macromolecular hydrodynamic radius in size exclusion chromatography. Benoit et al discovered that for a given solvent and column temperature, two different polymer molecules elute from a gel permeation column at the same time provided that the product of intrinsic viscosity $[\eta]$ and molecular weight M is the same. Thus, if a column is calibrated by using $\log(M^*[\eta])$ vs. elution volume at a given temperature, with a set of standard polymer samples whose molecular weight and intrinsic viscosity are known, one can determine the molecular weight of a unknown polymer from the observed retention volume and measured intrinsic viscosity.

When we run SEC-Viscotek system in the TriSEC GPC-Viscometry mode, it enables us to calculate data using the Universal Calibration approach, which is based on separation by the molecular size of the polymer. By calibrating the column elution to the log(M*[η]) of known standards and calculating the [η] of an unknown sample by using an on-line viscometer, we can generate a true molecular weight regardless of polymer structure.

B. SEC-Viscotek system set up

The universal calibration SEC molecular weight measurements are performed with a Viscotek Model 200 Differential Refractometer and Viscometer System. The other instruments in our system include Viscotek 222 HPLC pump, two Jordi Gel DVB mixed bed HPLC columns, and Viscotek DM400 data manager instrument. The effluent is monitored by two detectors, which are situated in parallel with one another at the outlet to the columns. The differential refractometer is used to determine the concentration of polymer as a function of the elution volume, the viscometer measures the intrinsic viscosity of the effluent. Then the molecular weight and molecular weight distribution of the eluting polymer are determined by the software based on the collected intrinsic viscosity information and concentration information.

The mobile phase is HFIP (1,1,1,3,3,3,-Hexafluoro-2-propanol) with saturated sodium trifluoroacetate (NaTFA). The samples are separated in two Jordi Gel DVB mixed bed HPLC columns at 40.0±0.1°C. The flow rate is 0.60ml/min.

C. Calibration

First, monodisperse PMMA standards have been run to calculate the mass constant, viscometer constant and peak parameters. The results are listed in Table 3.5.

Table 3.5: Instrumental Parameters for SEC-Viscotek.

Parameters	Value
Mass constant	3570
Viscometer constant*	0.500
RI Detector: Sigma (ml)	0.409
RI Detector: Tau (ml)	0.492
Viscosity Detector: Sigma (ml)	0.409
Viscosity Detector: Tau (ml)	0.467
Visc. Offset (ml)	-0.100

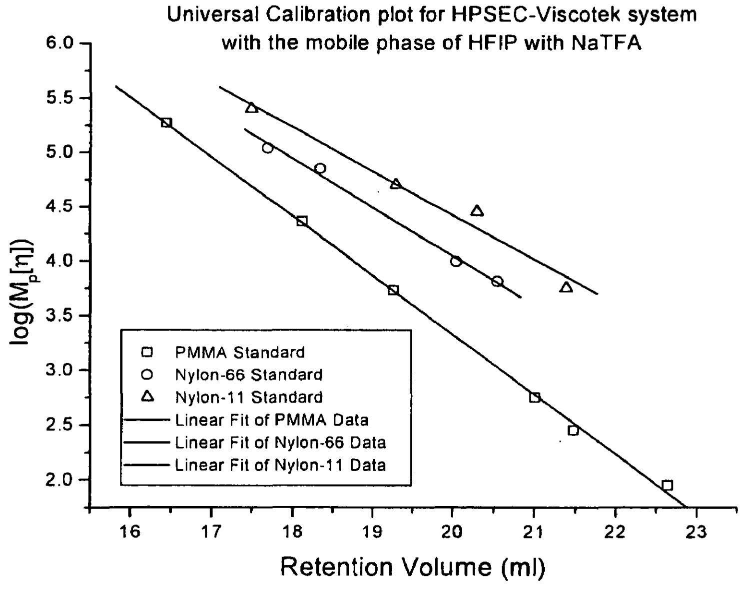
* Viscometer Constant was not measured directly from the narrow dispersed PMMA samples since corresponding intrinsic viscosity data were not available. Instead, we determined this value from three reference polymer samples with known intrinsic viscosity measured by Viscotek Company.

Second, the column was calibrated with standards of known molecular weight PMMA, polyamide-66 and polyamide-11. The PMMA and polyamide-66 samples are commercial standards. The Mp, Mn, Mw data supplied from the company were used for calibration. The polyamide-11 standards are fresh unplasticized sample #060799 and #061799 made in the lab. The Mw of the two samples are measured by HPSEC-LS in the lab. The Mn is assumed to be the one half of the Mw. For narrow dispersed PMMA samples, each run was corresponding to one point in the calibration plot, using the "Narrow Std Calibration" mode of the software. For broad dispersed polyamide-66 and polyamide-11 samples, each run accounted for two points in the calibration plot by using "Broad Std. Calibration" mode of the software. By inputting the reported the software then will generated two points with corresponding Mp, EV and [η] (different from input ones). The results are listed in the table 3.6. A calibration plot is presented in the figure 3.1.

Table 3.6: Universal Calibration of HPSEC-Viscotek System

Sample Description	Mp (kg/mol)	Elution Volume (ml)	Intrinsic Viscosity [ml/g]	Log(Mp[η])
PMMA1	2.4	22.64	0.037	1.95
PMMA2	4.9	21.47	0.058	2.45
PMMA3	6.9	21.00	0.082	2.75
PMMA6	28.9	19.26	0.187	3.73
PMMA7	69.0	18.12	0.329	4.36
PMMA8	212.0	16.44	0.886	5.27
Polyamide-66	12.8	20.54	0.498	3.81
Polyamide-66	15.2	20.04	0.645	3.99
Polyamide-66	52.4	18.34	1.345	4.85
Polyamide-66	66.5	17.69	1.660	5.04
Polyamide-11	10.6	21.38	0.531	3.75
Polyamide-11	29.5	20.29	0.955	4.45
Polyamide-11	47.0	19.29	1.053	4.70
Polyamide-11	118.3	17.49	2.129	5.40

Figure 3.1: Universal Calibration plot for HPSEC-Viscotek System with the mobile phase of HFIP with NaTFA



D. Accuracy checking:

Figure 3.1 suggests that both polyamide-66 and polyamide-11 in HFIP with NaTFA do not fall on the universal calibration curve for the PMMA standard. If we used the PMMA calibration plot to measure the polyamide-66 standards and fresh unplasticized polyamide-11 samples, the results had large deviation from the reported molecular weight or molecular weight measured by the HPSEC-LS in the lab. The results are presented in table 3.7.

Table 3.7: Molecular weight measurement of polymer standards by HPSEC-LS

Sample	Company Reported				Measured	HPSEC-Viscotek Measured		
	GPC Mp (kg/mol)	GPC Mn (kg/mol)	GPC Mw (kg/mol)	GPC Mw/Mn	LS Mw (kg/mol)	Mn (kg/mol)	Mw (kg/mol)	Mw/Mn
Polyamide-66, A	24.7	17.5	35.0	2.00	35.1±0.5	2.9	8.1	2.79
Polyamide-66, B	31.0	20.8	46.2	2.22	47.5±1.0	4.0	16.6	4.15
Polyamide-11	NA	NA	NA	NA	30.0±0.6	0.9	2.8	3.11
Polyamide-11	NA	NA	NA	NA	77.8±1.1	1.2	15.4	12.8

So we suggest the universal calibration SEC-Viscotek system with the mobile phase of HFIP with NaTFA does not provide an accurate molecular weight measurement of polyamide-11.

III. Conventional calibration SEC

A. Conventional calibration SEC set up and basic principles

Conventional calibration is based on a single concentration detector (interferometric refractometer) and calibrates the column elution (EV) with log of the molecular weight (logM vs. EV). Although it has the advantage of simplicity, typically calibrating to logM does not result in accurate absolute molecular weights except when the unknown samples have the same structure as the standards.[11]

The conventional calibration SEC has been set up for both systems in order to understand the effect of NaTFA in the mobile phase of HFIP. For HPSEC-LS system in HFIP without salt, we export the concentration vs. elution volume data to a data file. After setting up the calibration plot using narrow dispersed PMMA standard samples, an in-house program (source code file "sec_simu.cpp" attached in Appendix II) written by me has been run to calculate the molecular weight and molecular weight distribution based on the concentration-EV data files. For HPSEC-Viscotek system in HFIP with salt, we use the TriSEC software package from the Viscotek Company to set up the conventional calibration plot and perform the measurement.

B. Calibration by standard PMMA

The monodisperse PMMA standards are used to set up the standard calibration plots.

We used the measured peak retention volumes and corresponding reported peak molecular weight, Mp, to buil d our calibration plot (logM vs. EV). The results for HPSEC-LS system in HFIP with NaTFA are listed in Table 3.8. The results for HPSEC-Viscotek system in HFIP without NaTFA are list in Table 3.9. Then both the first order linear fit and third order polynomial fit have been used to obtain the correlation equations between logM and EV. The calibration plots for

HPSEC-LS system and HPSEC-Viscotek system are presented in Figure 3.2 and Figure 3.3, respectively.

Table 3.8: Retention Volume vs. Mp of PMMA, conventional calibration of HPSEC-LS system with mobile phase of HFIP without NaTFA

Sample Description	Company Reported Mp (kg/mol)	Measured Peak Retention Volume (ml)			
		03/20/00 Run in HFIP	03/24/00 Run in HFIP	03/28/00 Run in m-cresol	06/26/00 Run in HFIP
PMMA1	2.4	24.48	24.47	24.87	24.46
PMMA2	4.9	NA	NA	24.11	23.47
PMMA3	6.9	NA	NA	23.44	22.85
PMMA4	10.0	22.00	22.17	22.61	22.38
PMMA5	22.7	19.94	20.14	20.68	20.58
PMMA6	28.9	19.25	19.37	19.99	19.98
PMMA7	69.0	17.12	17.16	18.39	17.78
PMMA8	212.0	15.07	14.91	15.35	14.93
PMMA9	910.5	13.92	13.62	14.48	13.00

Table 3.9: Retention Volume vs. Mp of PMMA, conventional calibration of HPSEC-Viscotek system with mobile phase of HFIP with NaTFA

Sample Description	Company Reported Mp (kg/mol)	Measured Peak Retention Volume (ml)
		06/26/00 in HFIP
PMMA1	2.4	22.64
PMMA2	4.9	21.47
PMMA3	6.9	21.00
PMMA5	22.7	19.74
PMMA6	28.9	19.26
PMMA7	69.0	18.12
PMMA8	212.0	16.44
PMMA9	910.5	14.44

Figure 3.2: LogMp vs. EV, conventional SEC calibration set-up for HPSEC-LS system with the mobile phase of HFIP

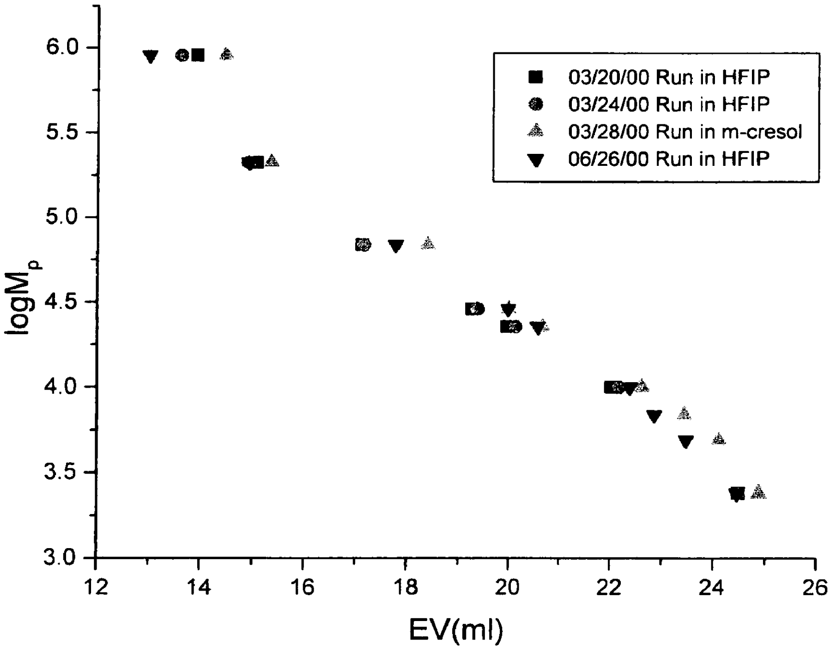
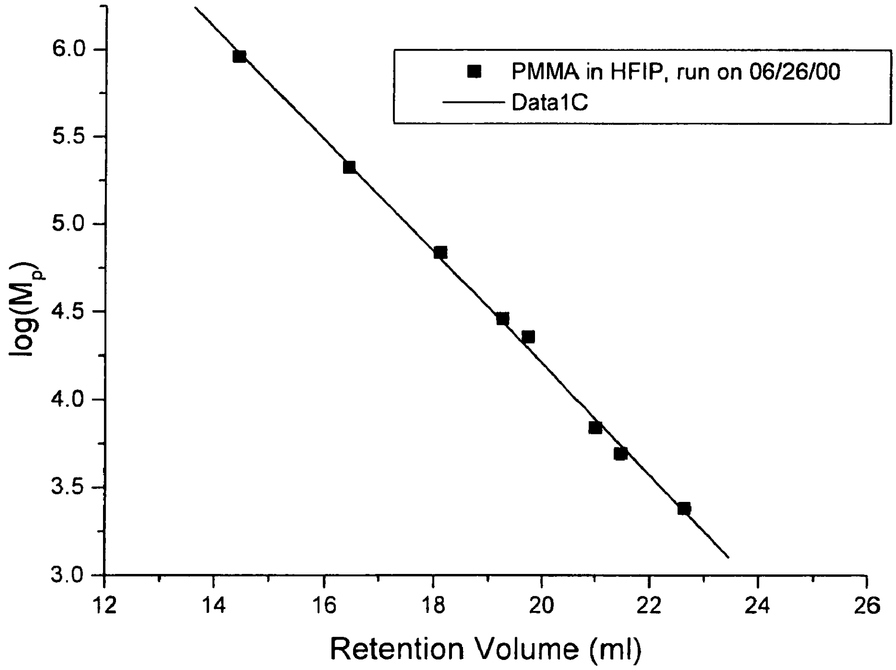


Figure 3.3: LogMp vs. EV, conventional SEC calibration set-up for HPSEC-Viscotek system with the mobile phase of HFIP with NaTFA



The figure 3.2 shows that for the same molecular weight PMMA standard, the elution volume shifted with time quite a bit. Thus frequent column calibration, if not daily, needs to be performed if one wants the reproducibility.

C. Programming and molecular weight measurement

In a HFSEC separation, it is generally assumed that each slice contains molecules of a single, or at least very narrow, molecular weight, M_i. Therefore, once a separation has been achieved and the collected data processed, the effective mass may be calculated over each peak selected from the following relations.[5]

Number average: $Mn = \Sigma c_i / \Sigma(c_i/M_i)$ (3.4)

Weight average: $Mw = \Sigma(c_i M_i)/\Sigma c_i$ (3.5)

Z average: $Mz = \Sigma(c_i M_i^2)/\Sigma(c_i M_i)$ (3.6)

Hence, M_i is the molecular weight of slice i at a concentration c_i. By importing the slice-by-slice details from the peak of RI signal of the polymer (concentration vs. elution volume), the program "sec_simu.exe" can calculate the M_i for each slice based on the calibration plot (logM vs. EV) based on PMMA standards. After integration, the program will output the number, weight and z-average molecular weight for each polymer run.

D. Accuracy checking

Using the conventional calibration plots by PMMA standards, the molecular weight of polyamide-66 standards and polyamide-11 samples were measured. For the HPSEC system in HFIP with NaTFA, each sample has been run at least twice during a month, the average and standard deviation has been calculated and tabulated in table 3.10.

Table 3.10: Molecular weight measurement, conventional calibration HPSEC system in HFIP with NaTFA

Sample	Company Reported				Measured	Conventional SEC, HFIP with NaTFA		
	GPC Mp (kg/mol)	GPC Mn (kg/mol)	GPC Mw (kg/mol)	GPC Mw/Mn	LS Mw (kg/mol)	Mn (kg/mol)	Mw (kg/mol)	Mw/Mn
Polyamide-66, A	24.7	17.5	35.0	2.00	35.4±0.2	15.9±2.0	29.4±4.5	1.85±0.3
Polyamide-66, B	31.0	20.8	46.2	2.22	47.5±1.0	18.4±4.5	52.1±12.1	2.9±0.7
Polyamide-11	NA	NA	NA	NA	30.0±0.6	9.5±1.8	19.0±2.7	2.0±0.1
Polyamide-11	NA	NA	NA	NA	77.8±1.1	14.2±2.9	56.7±5.7	4.1±0.8

For the HPSEC system in HFIP without NaTFA, the results are presented in table 3.11.

Table 3.11: Molecular weight measurement, conventional calibration HPSEC system in HFIP without NaTFA

Sample	Company Reported				Measured	Conventional SEC, HFIP without NaTFA		
	GPC Mp (kg/mol)	GPC Mn (kg/mol)	GPC Mw (kg/mol)	GPC Mw/Mn	LS Mw (kg/mol)	Mn (kg/mol)	Mw (kg/mol)	Mw/Mn
Polyamide-66, A	24.7	17.5	35.0	2.00	35.4±0.2	29.3±8.6	62.1±11.7	2.3±0.9
Polyamide-66, B	31.0	20.8	46.2	2.22	47.5±1.0	42.8±12.4	93.1±13.5	2.2±0.3
Polyamide-11	NA	NA	NA	NA	30.0±0.6	35.4±0.6	48.2±2.4	1.4±0.1
Polyamide-11	NA	NA	NA	NA	77.8±1.1	36.9±9.0	60.8±7.3	1.7±0.2

The table 3.10 and 3.11 show that the molecular weights of polyamide-11 and polyamide-66 measured in HFIP either with NaTFA or without NaTFA deviate greatly (from 10% to 94%!) from the company reported values, or our light scattering data. And the precision of the data is poor. The data suggest that conventional calibration SEC based on PMMA standards can not provide an accurate and reproducible measurement of molecular weight of polyamide-11 and polyamide-66. The assumption that the polyamide samples have the same elution time as PMMA standards when their molecular weights are identical is not dependable.

References for Chapter 3

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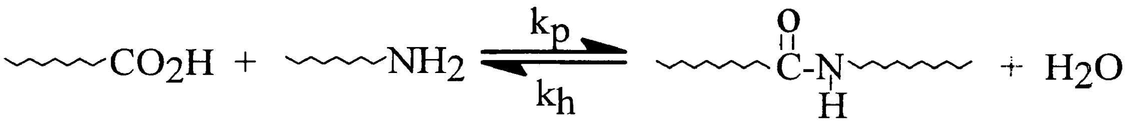
Chapter 4: Hypothesis and the mathematical model

The objective of this chapter is to develop a model for the degradation kinetics of polyamide-11. Earlier work showed the degradation kinetics consisted of a combination of two first order kinetic processes, one rapid and one much slower.[1] Our most recent work suggests that the degradation process approaches an equilibrium between hydrolysis-chain scission and polymerization-recombination.

I. Reaction Involving Chain Scission Rate Constant k_h and Recombination Rate Constant k_p:



$$\sim\sim CO_2H + \sim\sim NH_2 \underset{k_h}{\overset{k_p}{\rightleftharpoons}} \sim\sim \overset{O}{\overset{\|}{C}}-\underset{H}{N}\sim\sim + H_2O$$

II. Hypothesis:

When the hydrolysis-chain scission happens to the amide unit, solid-state polymerization or recombination can also happen as the acid end groups combine with the amine end groups. Equilibrium is approached where the reaction rate of degradation-hydrolysis equals the reaction rate of recombination-polymerization.

III. Assumption:

A. Concentration of acid chain end groups and amine chain end groups are equal, $[R_2NH_2]=[R_1CO_2H]$. Since polyamide-11 is made from step condensation of monomer (11-aminoundecanoic acid), there is a 1:1 ratio of acid end groups vs. amine end groups throughout the polymerization. Then if hydrolysis-chain scission of the amide group is the main degradation mechanism, breaking of one amide group should result in one acid end group and one amine end group. Thus the concentration of acid end groups should be equal to the amine end groups at all times, and this assumption is reasonable based on our degradation mechanism and hypothesis.

B. The amide concentration [-NHCO-] is large and may be assumed to be constant. This assumption is reasonable when we consider hydrolysis vs. the solid-state polymerization reaction. For example, assuming the Mw of polyamide-11 is 60000 and Mw/Mn=2, which is common for commercial pipe, then the Mn of polyamide-11 should be around 30000. Thus there are about 150 amide units per chain. After degradation, if Mn decreases to 10000, hydrolysis-chain scission should happen in two amide units per chain. The change of concentration of amide unit is just 2/150=1.33%, not a large amount.

C. Water concentration is large and approximately constant. This means that we assume at a given temperature the water diffusion is much faster than the hydrolysis-recombination reaction, considering the small water molecule has much higher mobility than the end groups which are attached to the long polymer chains. So the overall reaction rate is not determined by water diffusion rate unless the polyamide-11 sample is very thick. We believe this assumption is reasonable based on the unpublished Wellstream Company's former study, where there was no gradient of water concentration observed in the polymer layer and typical water concentrations in the temperature region of interest were between 2~3% by weight.[2] This assumption is also valid based on the paper of J. Verdu[3] in Polymer which shows water diffusion occurs over a matter of a few days for samples with 1cm or less in thickness for the temperatures of 90°C to 120°C used in this work. It is true that water concentration should be different at the different temperatures and could depend on the crystallinity of the polyamide-11 samples. Any changes of water concentration will lead to differences in the fit of the model.

D. The influence of plasticizer is neglected. We made polyamide-11 from the monomer, without any plasticizer. In the future we are going to compare the aging of unplasticized polyamide-11 degradation with the aging of plasticized nylon, in the same aging environment and determine if there is an effect of plasticizer on the polyamide-11 degradation rate.

IV. Nomenclature:

1. c_t – concentration of either amine ends group [-NH_2] or acid ends group [-CO_2H] at the time t, unit: $mol \cdot l^{-1}$
2. c_i - the initial concentration of either kind of end group, unit: $mol \cdot l^{-1}$

3. c_e – the concentration of either kind of end group when system reaches equilibrium, unit: mol·l^{-1}
4. a_t – the fraction of the remaining end group (either [-NH$_2$] or [-CO$_2$H]) at the time of t, unitless
5. a_i - the initial fraction of the remaining end group, unitless
6. a_e – the fraction of the remaining end group when system reaches equilibrium, unitless
7. k_p – rate constant for solid state polymerization, unit: l·mol^{-1}·s^{-1}
8. k_h – rate constant for hydrolysis, unit: l·mol^{-1}·s^{-1}
9. M_0 – the molecular weight of the repeating unit in polyamide-11, unit: kg·mol^{-1}
10. m – the mass of the initial system, unit: kg
11. V – the volume of the system , unit: l
12. D – density of the system, unit: kg·l^{-1}
13. [-NHCO-] – the concentration of amide group in the system, unit: mol·l^{-1}
14. [H$_2$O] – the concentration of "effective" water inside the solid polyamide-11 semi-crystalline system, unit: mol·l^{-1}
15. A_p – Arrhenius frequency factor for solid state polymerization, unit: J·mol^{-1}
16. E_p – Activation energy for solid state polymerization, unit: l^3·mol^{-1}·s^{-1}
17. A_h – Arrhenius frequency factor for hydrolysis reaction, unit: J·mol^{-1}
18. E_h – Activation energy for hydrolysis, unit: l^3·mol^{-1}·s^{-1}

V. Derivation:

$$-\frac{d[-NH_2]}{dt} = -\frac{d[-CO_2H]}{dt} = k_p[-CO_2H][-NH_2] - k_h[-NHCO-][H_2O] \tag{4.1}$$

When system reaches equilibrium,

$$-\frac{d[-NH_2]}{dt} = -\frac{d[-CO_2H]}{dt} = 0,$$

Then

$$k_p[-CO_2H]_e[-NH_2]_e = k_h[-NHCO-]_e[H_2O]_e$$

And

$$[-NHCO-]_e[H_2O]_e = k_p c_e^2 / k_h \tag{4.2}$$

Since we assume [-NHCO-] and [H_2O] are constant, at any time t, it follows

$$[-NHCO-][H_2O] = k_p c_e^2 / k_h \tag{4.3}$$

Equations (4.1) and (4.3) yield

$$-\frac{dc}{dt} = k_p(c^2 - c_e^2) \tag{4.4}$$

or

$$-\frac{dc}{c^2 - c_e^2} = k_p dt \tag{4.5}$$

Integrating t from 0 to t, integrating c from c_i to c

$$\int_{c_i}^{c} -\frac{dc}{c^2 - c_e^2} = \int_0^t k_p dt \tag{4.6}$$

Hence,

$$c_t = Ce\frac{-1+\frac{Ce+Ci}{Ce-Ci}e^{2cekpt}}{1+\frac{Ce+Ci}{Ce-Ci}e^{2cekpt}} \tag{4.7}$$

Then define the product of the amide bonds concentration and water concentration as B, recalling this product is approximated as constant. $[-NHCO-]_t[H_2O]_t = B$, and from Equation (4.3) one obtains

$$c_e = \sqrt{\frac{Bk_h}{k_p}} \tag{4.8}$$

Equation (4.7) can be written as:

$$c_t = Ce\frac{-1+\frac{Ce+Ci}{Ce-Ci}e^{2\sqrt{Bk_hk_p}t}}{1+\frac{Ce+Ci}{Ce-Ci}e^{2\sqrt{Bk_hk_p}t}} \tag{4.9}$$

define

$$J = 2\sqrt{Bk_hk_p} = 2\sqrt{k_hk_p[-NHCO-][H_2O]} \tag{4.10}$$

Equation (4.9) can be written as:

$$c_t = Ce\frac{-1+\frac{Ce+Ci}{Ce-Ci}e^{Jt}}{1+\frac{Ce+Ci}{Ce-Ci}e^{Jt}} \tag{4.11}$$

since for step condensation reaction

$$c = \frac{am/Mn}{V} = \frac{am/\frac{M_0}{1-p}}{V} = \frac{a^2m}{VM_0} \tag{4.12}$$

Equation (4.11) turns into

$$a_t = a_e\left(\frac{-1+\frac{a_e^2+a_i^2}{a_e^2-a_i^2}e^{Jt}}{1+\frac{a_e^2+a_i^2}{a_e^2-a_i^2}e^{Jt}}\right)^{0.5} \tag{4.13}$$

Using

$$Mn = \frac{M_o}{a} \qquad \text{Where } a=1\text{-}p \tag{4.14}$$

$$Mw = M_0 \frac{1+p}{1-p} = M_0(\frac{2}{a} - 1) \approx M_0 \frac{2}{a} \tag{4.15}$$

we obtain

$$Mn_t = Mn_e \left(\frac{1+\frac{Mn_i^2 + Mn_e^2}{Mn_i^2 - Mn_e^2} e^{Jt}}{-1+\frac{Mn_i^2 + Mn_e^2}{Mn_i^2 - Mn_e^2} e^{Jt}} \right)^{0.5} \tag{4.16}$$

$$Mw_t = Mw_e \left(\frac{1+\frac{Mw_i^2 + Mw_e^2}{Mw_i^2 - Mw_e^2} e^{Jt}}{-1+\frac{Mw_i^2 + Mw_e^2}{Mw_i^2 - Mw_e^2} e^{Jt}} \right)^{0.5} \tag{4.17}$$

VI. Discussion:

A. Objective Function:

An optimal parameter estimation program has been developed by using Microsoft Visual C++. (Attached Source Code File: Aging_simulation.cpp) The program has been run to obtain the best-fit values of Mw_e and J for the proposed equation by using the experimental molecular weight data of the aging polyamide-11 study. A repetitive algorithm has been used where the objective function that has been minimized is given by

$$F(x) = \sqrt{\frac{\sum_{i=1}^{N} \left| Mw,_{\exp}(i) - Mw,_{theory}(i) \right|^2}{N-1}} \tag{4.18}$$

Another objective function we are using to minimize the relative deviation is given by

$$F'(x)=\sum_{i=1}^{N}\frac{\left|Mw,_{\exp}(i)-Mw,_{theory}(i)\right|}{Mw,_{theory}(i)} \tag{4.19}$$

B. Equations for Mw_e and J

Equations (4.8), (4.12), (4.15) yields

$$Ce=\sqrt{\frac{[-NHCO-][H_2O]k_h}{k_p}}=\frac{a_e^2m}{M_0V}=\frac{\left(\frac{2M_0}{Mw_e}\right)^2D}{M_0} \tag{4.20}$$

Where D=m/V,

Rearranging Equation (4.20), we obtain

$$Mw_e=\frac{2\sqrt{M_0D}}{\sqrt[4]{\frac{k_h}{k_p}[-NHCO-][H_2O]}} \tag{4.21}$$

while Equation (4.10) gives us

$$J=2\sqrt{k_hk_p[-NHCO-][H_2O]} \tag{4.22}$$

Equation (4.21) suggests that the molecular weight of the polyamide-11 will reach equilibrium at a given temperature, regardless of the initial molecular weight. Since the density of polyamide-11 is relatively constant in the range of molecular weights examined, and we assume that [-NHCO-] and $[H_2O]$ are constant, then Mw_e should only depend on the ratio of k_h/k_p.

Equation (4.22) suggests that at the same aging temperature, the values of J which are determined from the best-fit method should be close to each other since J only depends on the product of $k_h k_p$.

C. Temperature dependence of Mwe and J

From the Arrhenius equation:

$$k_h = A_h e^{-E_h/RT} \tag{4.23}$$

$$k_p = A_p e^{-E_p/RT} \tag{4.24}$$

Equation (21) can be written as

$$Mw_e = \frac{2\sqrt{M_0 D}}{\sqrt[4]{\frac{A_h}{A_p} e^{-\frac{E_h - E_p}{RT}} [-NHCO-][H_2O]}} \tag{4.25}$$

Equation (22) can be written as

$$J = 2\sqrt{A_h A_p e^{-\frac{E_h + E_p}{RT}} [-NHCO-][H_2O]} \tag{4.26}$$

Using the experimental data at each temperature (120°C, 105°C, and 90°C), the temperature dependence of Mw_e ($Mw_e(T)$ vs. T) and J (J(T) vs. T) can be determined. Hence, for a given temperature, we can determine the values of Mw_e and J from these plots and then by using the equation (4.17), it is possible to predict the molecular weight of polyamide-11 after aging at any given time, and at any given temperature within the temperature range studied.

References for Chapter 4

1. D. K. Hood, "Monitoring and Modeling of Infiltration, Polymerization, and Degradation Phenomena in Polymeric Systems," Ph.D. Dissertation, College of William and Mary, 1996
2. Unpublished Joint Report for Rilsan User Group Meeting on Hydrolysis, June 10, 1999.
3. G. Serpe, N. Chaupart, J. Verdu, *Polymer*, 1997, **38**, 1911.

Chapter 5: Experimental results

I. Sample Preparation

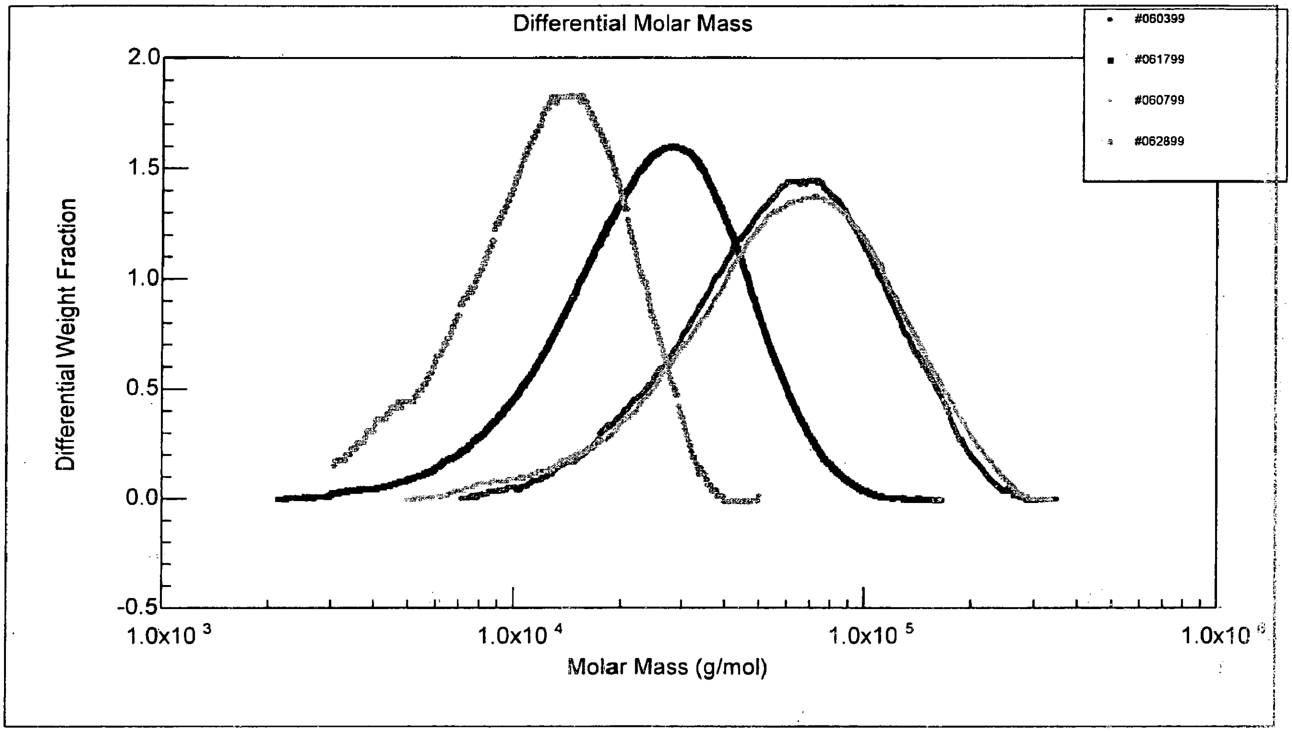
The ω-aminoundecanoic acid was purchased from Aldrich Co. The unplasticized polyamide-11 was prepared by melt polymerization of the amino acid at ca. 200°C under Argon.[1] The polymerization times were controlled to get different molecular weight samples. The thermal history of each polymer is listed in table 5.1.

Table 5.1: Thermal History and LS molecular weight of Unplasticized polyamide-11

Sample Description	Mw (kg/mol)	Thermal History
Unplasticized polyamide-11, #060399	72.0±1.2	The polymer was made by melt polymerization at ca. 195°C under about a 15 inch Hg vacuum, for about 12 hrs. Argon flux inside the oven during the whole procedure.
Unplasticized polyamide-11, #060799	77.8±1.1	The polymer was made by melt polymerization at ca. 195°C under about a 15 inch Hg vacuum, for about 12 hrs. Argon flux inside the oven during the whole procedure. After that the polymer was quenched in liquid N_2.
Unplasticized polyamide-11, #061799	30.0±0.6	The polymer was made by melt polymerization at ca. 190°C under about a 15 inch Hg vacuum, for about 1.5 hrs. Argon flux inside the oven during the whole procedure.
Unplasticized polyamide-11, #062899	14.8±0.7	The polymer was made by melt polymerization at ca. 190°C under about a 15 inch Hg vacuum, for about 45 min. Argon flux inside the oven during the whole procedure

The differential molecular weight distribution plots of these unplasticized polyamide samples are shown in figure 5.1.

Figure 5.1: Differential molecular weight distribution for fresh unplasticized polyamide
From right to left: #060799, #060399, #061799, #062899



We see unimodal Gaussian shaped peaks for fresh unplasticized polyamide-11. It suggests HFIP is a good mobile phase for polyamide-11 in our HPSEC-LS system even without adding NaTFA.

II. Aging Environment

The unplasticized nylon samples with different molecular weights are cut into a uniform dimension bars, or uniform size pellets punched from the polymer panels. These bars or pellets are placed in Acer pressure tubes in pure deionized water under argon. Then they were put into the air oven at 70.0±0.1°C, 80.0±0.1°C, 90.0±0.1°C, 105.0±0.1°C and an oil bath of 120.0±0.1°C. The temperatures are monitored by thermometers. After aging for certain periods of time, samples are taken from the environment, cut and dried. Then they are dissolved in *meta*-cresol and molecular weight measurements are made.

III. Experimental Results

A. LS Data

The molecular weight data have been collected from HPSEC-LS system with the mobile phase of HFIP. The results of aging of unplasticized polyamide-11 in 100% DI water with Argon in 120°C, 105°C and 90°C(still in progress) are listed in Table 5.2, Table 5.3 and Table 5.4 respectively.

Table 5.2 Molecular weight measurement of aging of unplasticized polyamide-11 in 120°C, 100%DIw/Ar

	#060799					#060399					#061799					#062899				
Aging Days	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$
0	53.4	77.9	116.7	1.46	1.50	53.9	72.4	103.2	1.34	1.43	24.2	30.1	40.8	1.24	1.36	11.8	14.6	21.0	1.24	1.44
5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	25.2	27.8	32.4	1.10	1.17	15.5	19.9	23.1	1.29	1.16
9	28.5	33.7	40.9	1.18	1.21	26.3	34.0	43.5	1.29	1.28	23.9	26.5	29.9	1.11	1.13	18.9	21.2	23.9	1.12	1.13
26	26.5	30.7	38.2	1.16	1.24	27.8	31.1	35.6	1.12	1.14	20.2	26.1	30.5	1.29	1.17	13.4	22.6	28.7	1.68	1.27
37	22.9	28.2	34.9	1.23	1.24	27.0	30.7	39.4	1.14	1.28	21.4	25.7	30.5	1.20	1.19	22.3	24.4	27.6	1.09	1.13
49	22.3	26.1	31.5	1.17	1.21	22.4	27.7	35.7	1.24	1.29	22.4	25.3	29.4	1.13	1.16	22.0	24.6	28.1	1.12	1.14
69	18.0	25.1	33.5	1.40	1.33	20.5	26.8	32.9	1.31	1.23	22.8	25.0	29.4	1.10	1.18	20.5	25.3	29.8	1.23	1.18
90	19.9	25.8	31.9	1.30	1.24	18.7	24.7	30.2	1.32	1.22	20.3	25.0	27.2	1.23	1.09	23.7	25.1	26.5	1.06	1.06

Table 5.3 Molecular weight measurement of aging of unplasticized polyamide-11 in 105°C, 100%DIw/Ar

	#060799					#060399					#061799					#062899				
Aging Days	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$
0	53.4	77.9	116.7	1.46	1.50	53.9	72.4	103.2	1.34	1.43	24.2	30.1	40.8	1.24	1.36	11.8	14.6	21.0	1.24	1.44
2	55.0	75.1	126.8	1.37	1.69	53.4	74.0	107.0	1.38	1.45	27.1	30.0	34.6	1.11	1.15	12.1	16.0	19.7	1.32	1.23
5	51.7	69.2	104.6	1.34	1.51	42.9	59.4	81.8	1.38	1.38	26.2	29.6	35.9	1.13	1.21	14.8	15.7	16.8	1.06	1.07
8	52.7	67.0	96.8	1.27	1.44	45.1	63.5	96.8	1.41	1.53	26.0	29.1	32.9	1.12	1.13	15.5	17.3	20.7	1.12	1.20
16	31.6	44.1	72.7	1.40	1.65	34.1	42.6	63.1	1.25	1.48	26.0	29.1	33.4	1.12	1.15	14.7	16.9	21.8	1.15	1.29
33	29.8	38.5	54.4	1.29	1.41	28.7	39.8	59.3	1.38	1.49	23.1	27.9	35.1	1.21	1.26	10.3	21.3	27.5	2.07	1.29
64	23.6	30.6	40.0	1.30	1.31	26.0	33.3	49.4	1.28	1.48	22.4	26.1	29.2	1.17	1.12	13.6	22.2	28.3	1.63	1.27
128	25.0	28.7	38.9	1.15	1.36	18.5	25.3	33.5	1.37	1.32	17.2	25.5	36.1	1.48	1.42	19.5	24.4	31.9	1.25	1.31
190	14.8	24.0	32.1	1.62	1.34	18.1	25.2	31.0	1.39	1.23	18.5	25.2	36.4	1.36	1.44	19.4	25.4	32.9	1.31	1.30
256	17.7	23.7	29.4	1.34	1.24	15.5	25.2	36.7	1.65	1.46	19.5	25.0	28.7	1.28	1.15	23.6	26.6	29.6	1.13	1.11

Table 5.4 Molecular weight measurement of aging of unplasticized polyamide-11 in 90°C, 100%DIw/Ar
(In Progress)

	#060799					#060399					#061799					#062899				
Aging Days	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$
0	53.4	77.9	116.7	1.46	1.50	53.9	72.4	103.2	1.34	1.43	24.2	30.1	40.8	1.24	1.36	11.8	14.6	21.0	1.24	1.44
5	45.8	62.4	91.6	1.36	1.47	48.1	65.4	90.3	1.36	1.38	24.7	29.3	34.7	1.19	1.18	15.9	17.6	20.3	1.15	1.11
33	32.9	47.6	79.2	1.45	1.66	35.1	52.9	74.9	1.51	1.42	23.8	29.4	34.2	1.24	1.16	15.5	19.5	23.4	1.26	1.20
65	30.3	41.7	63.9	1.38	1.53	32.5	49.7	69.7	1.53	1.40	22.7	26.3	34.0	1.16	1.29	16.5	20.3	23.3	1.23	1.15
125	30.1	39.7	61.0	1.32	1.54	33.9	45.2	68.6	1.33	1.52	21.7	25.7	29.8	1.18	1.16	18.7	21.6	24.3	1.16	1.13
175	25.8	32.4	45.9	1.26	1.42	26.2	37.1	57.6	1.42	1.55	20.5	25.0	29.2	1.22	1.17	19.9	22.4	25.4	1.13	1.13

B. Fitting the molecular weight data with the mathematical model

The weight average molecular weight (Mw) from HPSEC-LS measurement of aging of each unplasticized polyamide-11 has been fit to equation (4.17) by using the optimal parameter estimation program. The best fit Mw_e and J for each starting polymer at each temperature has been calculated and tabulated. By using objective function (4.18), the results are shown in table 5.5. By using objective function (4.19), the results are shown in talbe 5.6. Based on the best fit Mw_e and J, the simulated molecular weight aging plot for each starting polymer at each temperature has been plotted with the experimental data in figure 5.2-17.

Table 5.5: The best fit parameters by using objective function equation (4.18)

		#060799	**#060399**	**#061799**	**#062899**
120°C	**M_i(kg/mol)**	77.9	72.4	30.1	14.6
	M_e(kg/mol)	26.8	27.9	25.3	24.6
	J (day^{-1})	1.28E-1	1.37E-1	1.24E-1	1.33E-1
	$F(x)_{min}$	1646	2082	331	777
105°C	**M_i(kg/mol)**	77.9	72.4	30.1	14.6
	M_e(kg/mol)	23.4	24.4	25.0	25.9
	J (day^{-1})	1.54E-2	1.73E-2	1.79E-2	2.25E-2
	$F(x)_{min}$	3817	3812	207	784

Table 5.6: The best fit parameters by using objective function equation (4.19)

		#060799	**#060399**	**#061799**	**#062899**
120°C	**M_i(kg/mol)**	77.9	72.4	30.1	14.6
	M_e(kg/mol)	26.0	27.7	25.3	24.6
	J (day^{-1})	1.27E-1	1.44E-1	1.21E-1	1.29E-1
	$F'(x)_{min}$	3.79%	4.99%	0.93%	2.12%
105°C	**M_i(kg/mol)**	77.9	72.4	30.1	14.6
	M_e(kg/mol)	23.5	24.4	25.0	26.1
	J (day^{-1})	1.82E-2	1.71E-2	1.70E-2	1.87E-2
	$F'(x)_{min}$	5.22%	4.86%	0.48%	3.2%

Figure 5.2: Unplasticized Nylon #060799 in 120°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.18).

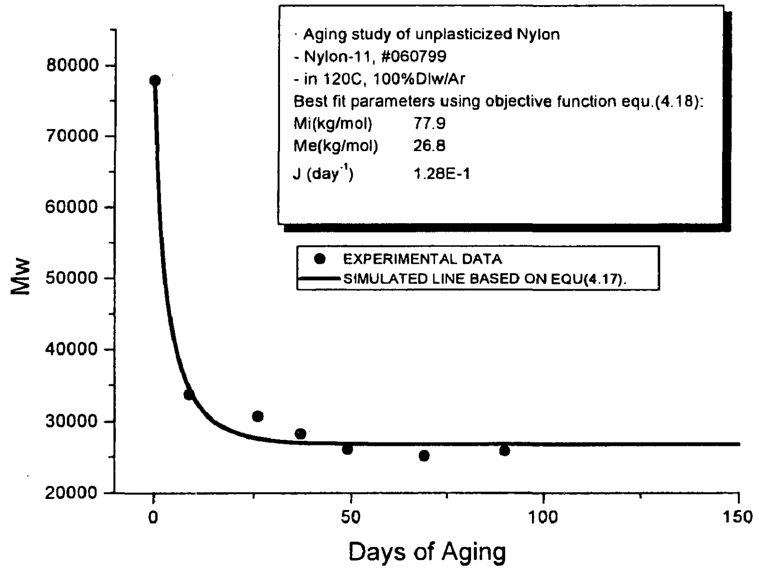


Figure 5.3: Unplasticized Nylon #060799 in 120°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.19).

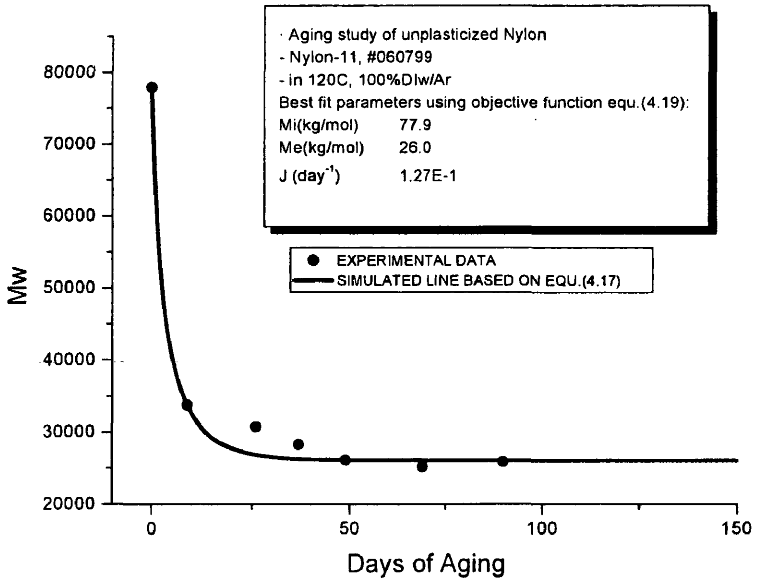


Figure 5.4: Unplasticized Nylon #060399 in 120°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.18).

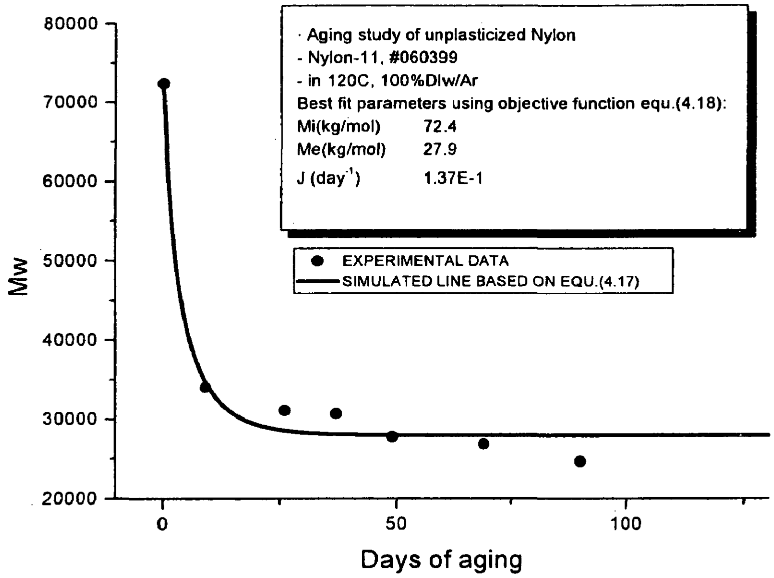


Figure 5.5: Unplasticized Nylon #060399 in 120°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.19).

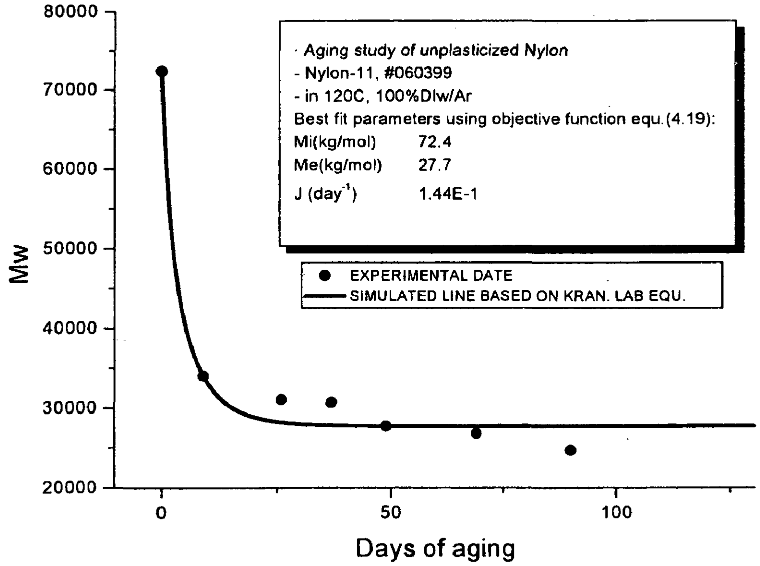


Figure 5.6: Unplasticized Nylon #061799 in 120°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.18).

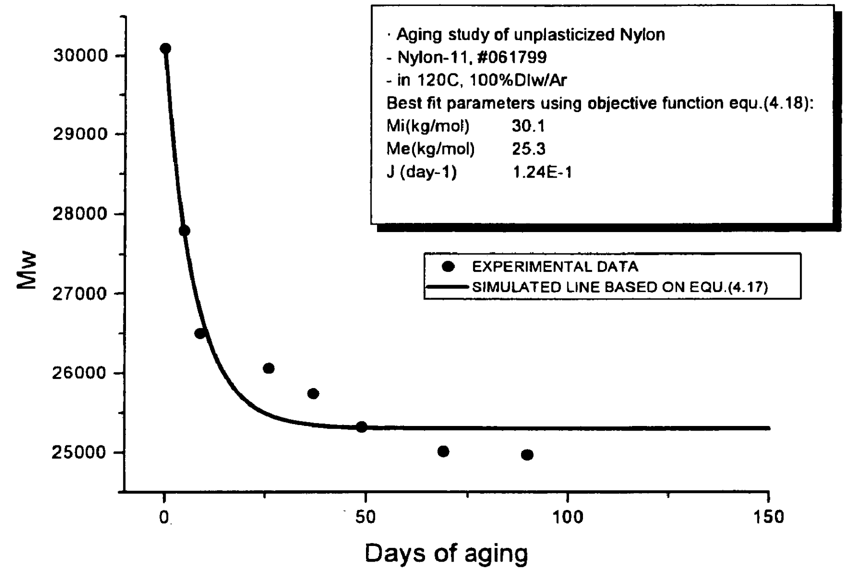


Figure 5.7: Unplasticized Nylon #061799 in 120°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.19).

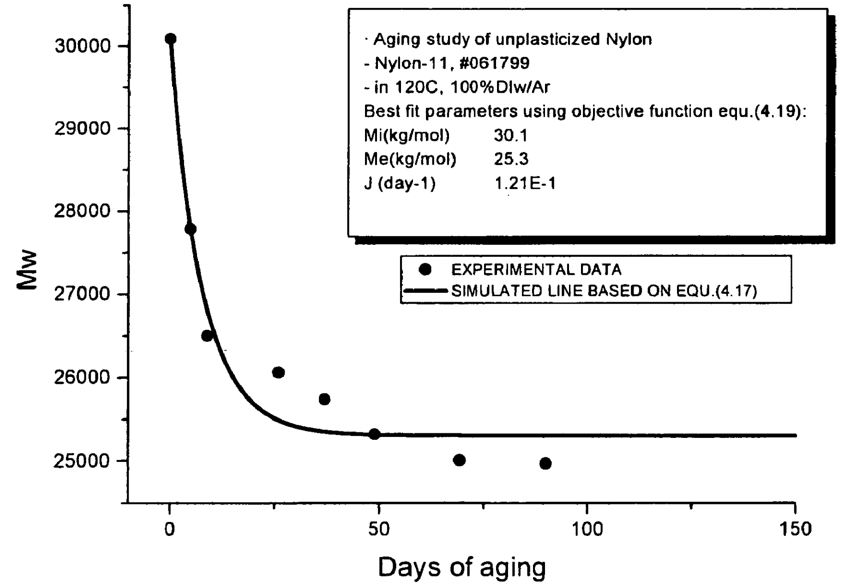


Figure 5.8: Unplasticized Nylon #062899 in 120°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.18).

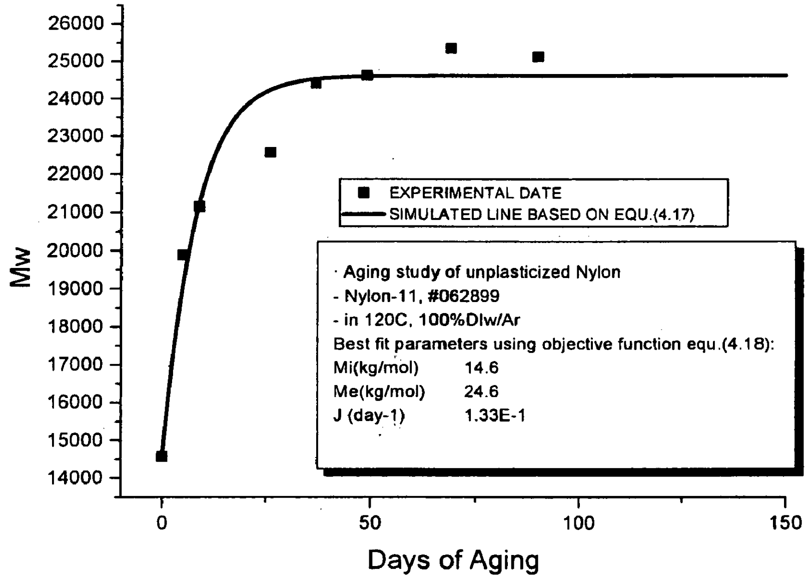


Figure 5.9: Unplasticized Nylon #062899 in 120°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.19).

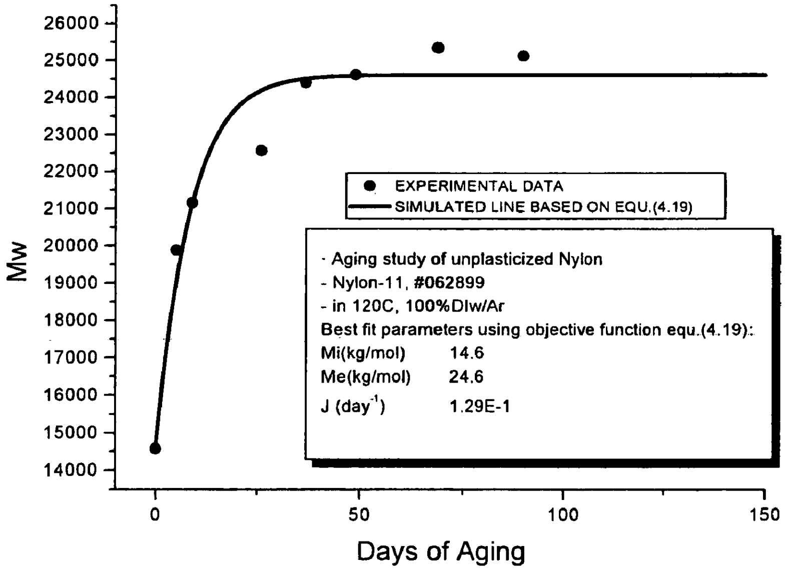


Figure 5.10: Unplasticized Nylon #060799 in 105°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.18).

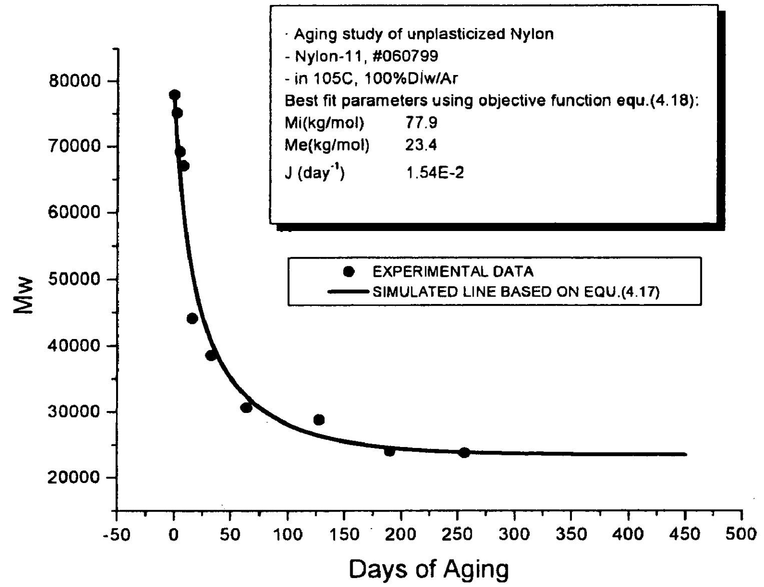


Figure 5.11: Unplasticized Nylon #060799 in 105°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.19).

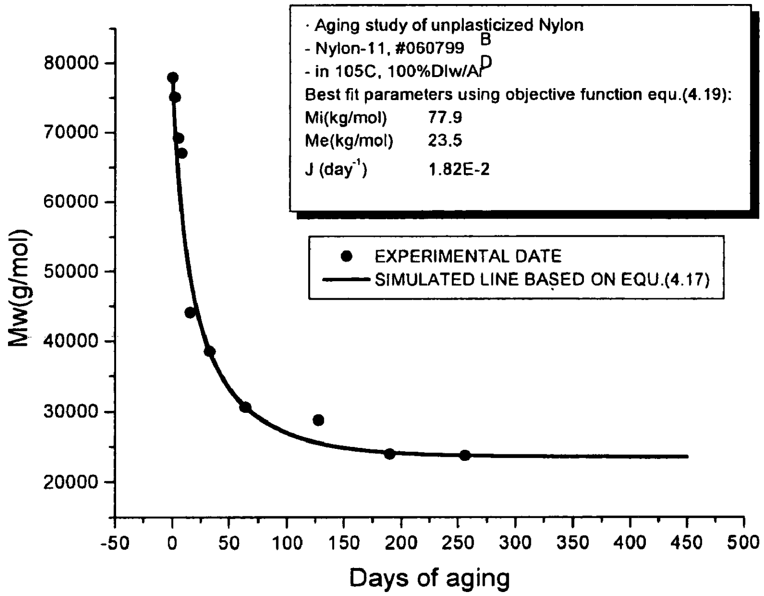


Figure 5.12: Unplasticized Nylon #060399 in 105°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.18).

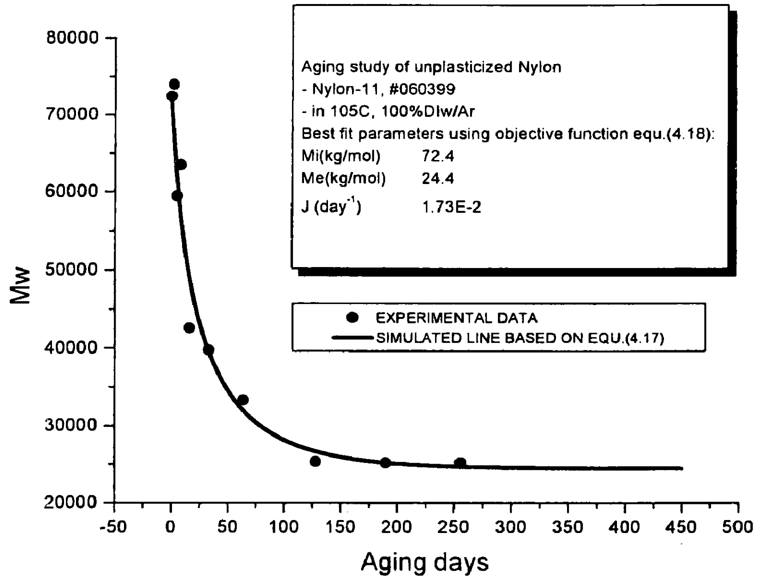


Figure 5.13: Unplasticized Nylon #060399 in 105°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.19).

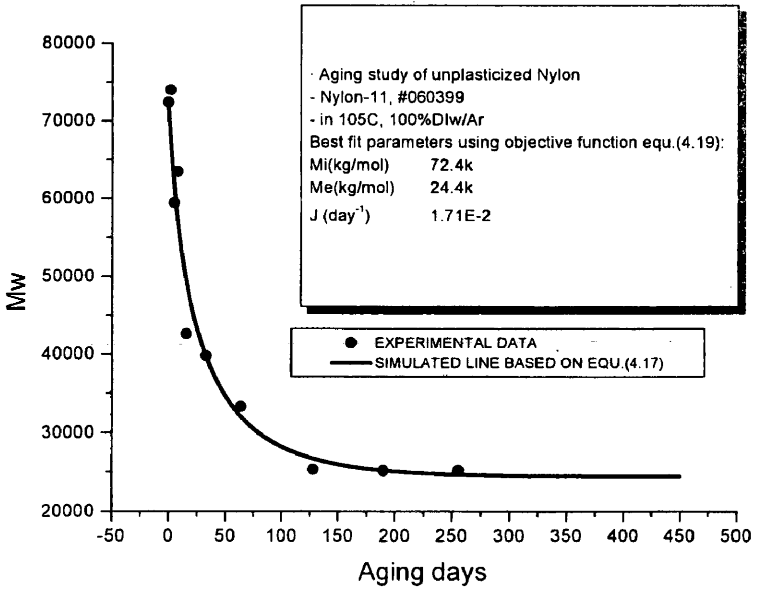


Figure 5.14: Unplasticized Nylon #061799 in 105°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.18).

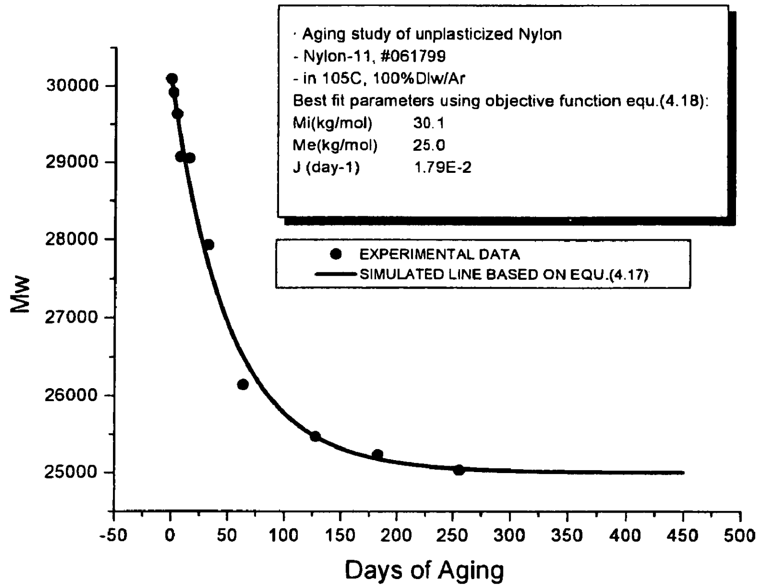


Figure 5.15: Unplasticized Nylon #061799 in 105°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.19).

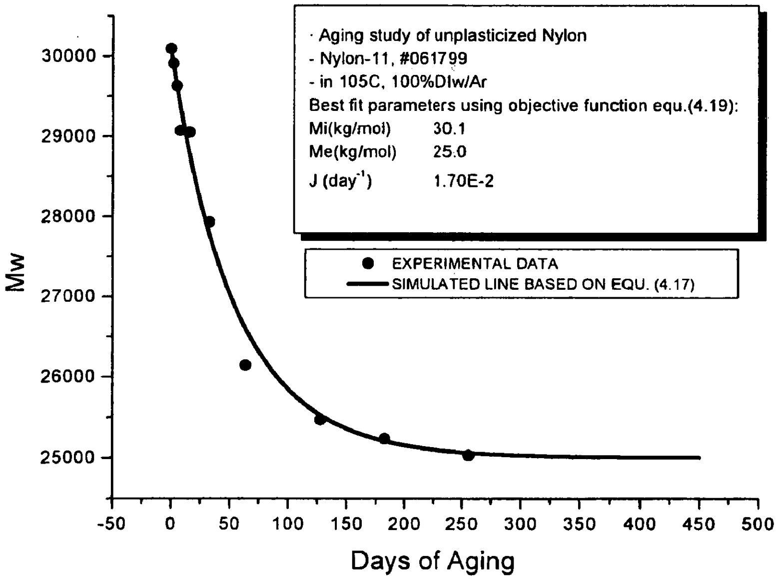


Figure 5.16: Unplasticized Nylon #062899 in 105°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.18).

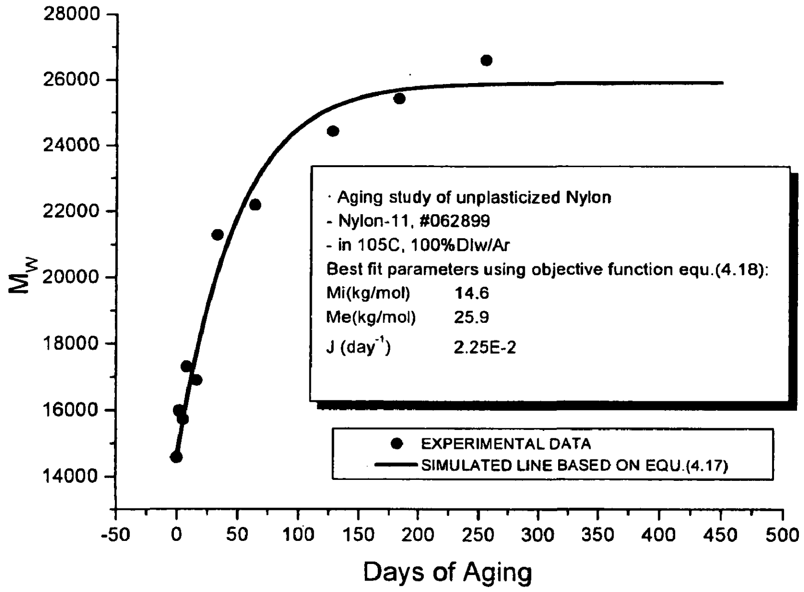
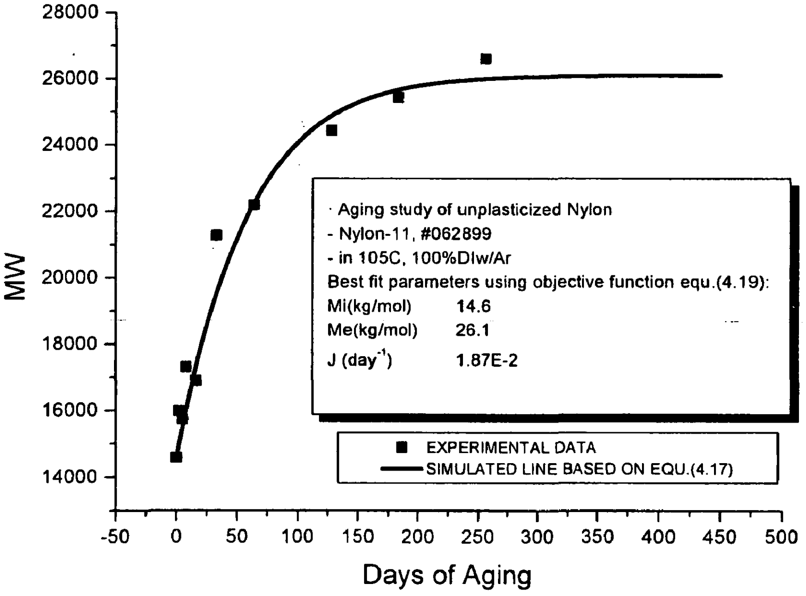


Figure 5.17: Unplasticized Nylon #062899 in 105°C, Mw vs. Aging Days, Experimental & Best Fit Simulated Plot based on Objective Function (4.19).



C. Temperature dependence of Mw_e and J

For each temperature, the average and standard deviation of Mw_e and J were calculated and presented in table 5.7.

Table 5.7: Data of Mw_e and J at the different temperatures

Aging Temperature	Objective Function	Average of Mw_e(kg/mol)	Standard Deviation of Mw_e	Average of J(day^{-1})	Standard Deviation of J
120°C	Equ. 4.18	26.2	1.5	0.131	0.006
	Equ. 4.19	25.9	1.3	0.130	0.009
105°C	Equ. 4.18	24.7	1.1	0.0183	0.0030
	Equ. 4.19	24.8	1.1	0.0178	0.0008

At the certain temperature, the average values of Mw_e and J by using either objective function are similar.

Equation 4.25 suggests ln(Mw_e) vs. 1/T should have a linear fit since we assume [-NHCO-] and [H_2O] are constant. Equation 4.26 suggests ln(J) vs. 1/T should have a linear fit as well. Since collection of LS data for 90°C aging study is still in progress, for now we can only use the results from 120°C and 105°C aging study to set up the temperature dependence plot of Mw_e and J. The plots are shown in figure 5.18 and 5.19 :

Table 5.8: ln(Mw_e) vs. 1/T, ln(J) vs. 1/T

Objective Function	1/T (K^{-1})	ln(Mw_e)	SD of ln(Mw_e)	ln(J)	SD of ln(J)
Equation 4.18	2.5436E-03	3.266	0.059	-2.033	0.046
	2.6445E-03	3.207	0.046	-4.001	0.178
Equation 4.19	2.5436E-03	3.254	0.051	-2.040	0.072
	2.6445E-03	3.211	0.045	-4.029	0.045

Figure 5.18: ln(Mw_e) vs. 1/T

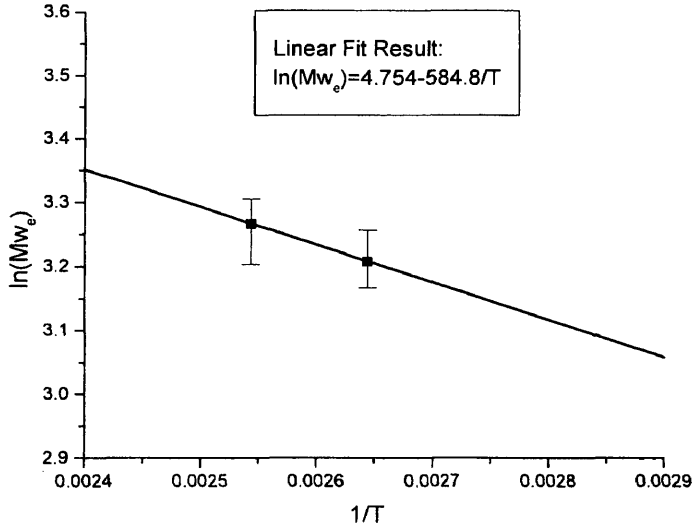
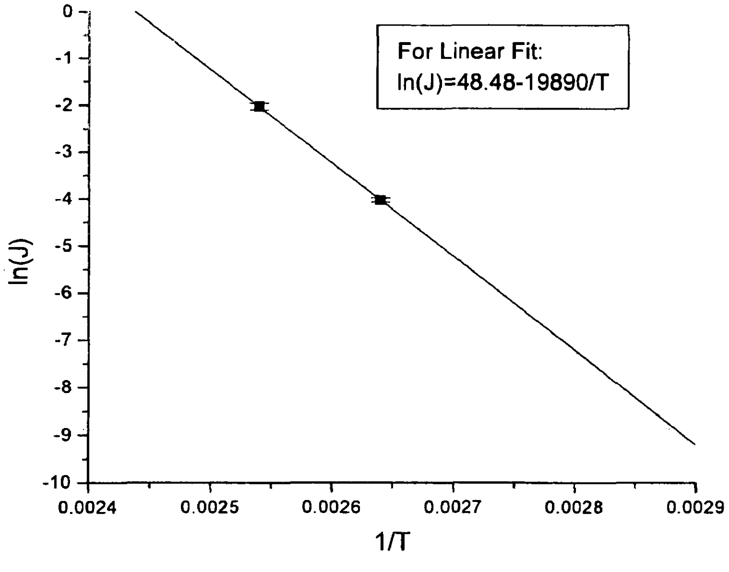


Figure 5.19: ln(J) vs. 1/T



References for Chapter 5

1. J. Zimmerman, "Polyamides", *Encyclopedia of Polymer Science and Engineering*, (H. F. Mark, N. M. Bicales, G. G. Overberger, and G. Manges, Eds.), Wiley-Interscience, New York, 1998, **11**, p. 370.

Chapter 6: Conclusions

I. HPSEC-LS system with the mobile phase of HFIP can accurately measure the absolute value of weight average molecular weight of polyamide-11 at room temperature. Thus this system provides us a convenient and sensitive means to monitor the aging of polyamide-11.

II. Compared with the HPSEC-LS method, conventional calibration SEC method is an inaccurate, and sometimes a poor method to measure the molecular weight of polyamide-11. First, since polyamide-11 standards are unavailable, PMMA standards are used to set up calibration plots and one has to assume the polyamide-11 samples have the same elution time as PMMA standards when their molecular weights are identical. Second, tremendous amounts of time are required for frequent column calibration, whenever a column has been replaced, the resolution of a column set deteriorates, or there is a slight change in solvent.

III. The universal calibration SEC-Viscotek system with the mobile phase of HFIP with NaTFA does not provide an accurate molecular weight measurement of polyamide-11. Both Nylon-66 and polyamide-11 in HFIP do not fall on the universal calibration curve for the PMMA standards.

IV. Using our HPSEC-LS system with the mobile phase of HFIP, we see unimodal Gaussian shaped peaks for fresh unplasticized polyamide-11 and Nylon-66 standard even without adding the salt (NaTFA) to the mobile phase.

V. At the each aging temperature of 120°C and 105°C (90°C in progress) in pure water environment, an equilibrium has been approached regardless of the molecular weight of the starting polymer. The weight average of molecular weight at equilibrium (Mw_e) for different starting materials was the same within the experimental error. This result proves our hypothesis, that the degradation process for polyamide-11 approaches an equilibrium between hydrolysis-chain scission and polymerization-recombination.

VI. Our mathematical model fits the weight average molecular weight data for aging of polyamide-11. Based on the best-fit methods, the reaction rate related parameter J was computed. The values of J at the given aging temperature are identical within the experimental error. The fact adds further credibility to our mathematical model.

VII. The Mw_e and J vs. temperature plots has been set up based on the studies on the aging of unplasticized polyamide-11 in pure water at the temperature of 120°C, 105°C. (90°C in progress). For a given temperature within this range, we can estimate the values of Mw_e and J from these plots. Hence, by using equation (4.17), it is possible to predict the molecular weight of polyamide-11 during aging in pure water at any time. The accuracy of the plots when extrapolated to lower temperature will be checked by the in-progress studies on the aging of polyamide-11 at the temperature of 80°C and 70°C.

VIII. The model only works for the aging of polyamide-11 in the pure water environment without oxygen. Our previous studies on the aging of polyamide-11 in an acid environment or alcohol (methanol, ethyl-glycol etc.) environment suggest different degradation rates and molecular weights when compared with the aging process in the pure water at the same temperature and time. Future studies will concentrate on the mechanism and kinetics of aging of polyamide-11 in the present of acid and alcohol. The model also needs to be modified to treat these more complicated environments.

IX. Finally, the role, if any, of the plasticizer in the aging of commercial polyamide-11 needs to be studied.

Appendix:

I. Aging_simulation.cpp

II. sec_simu.cpp

```
//************************************************************************
// Program: aging_simulation.cpp
// Author:  Yao Lin
// Research Advisor: Dr. D. E. Kranbuehl
// Version: 0.99 beta
// Last Revised Date: 06/10/2000
// Project:        Aging study of Unplasticized Nylon-11 in 100%DIw/Ar at the
//                 temperature of 120C, 105C, 90C, 80C, 70C
// Objective:      Using the least square best fitting method to fit the experimental
//                 data with the simulated plot based on our theoritical equation,
//                 and return the two best fit parameters, which are MW_E and A.
// Comment:        Brutal force aglorithm has been used to search a "LOCAL" best fit
//                 parameters.
//Bad News:        In two cases, the program might fail: first, if the
//                 experimental data deviates from the trend of theoritical model too
//                 much; second, you give a unresonable range of guessA, which might
//                 lead the program approach a local best fit parmeters you are not
//                 interested on. So two tips: first, after you get the results, use
//                 Origin software to simulate the theoritical equation by using the
//                 best fit parameters you just get, and compare with the experimental
//                 data, chi-by-eye; second, don't set up a too broad range of guessA,
//                 instead, you can try several range of guessA one by one, and compare
//                 with the results, trial-and-error. Good Luck.
// Good News:      For nylon-11 degradation study, the resonable guessA should be
//                 set between 0.0 and 1.0. I am positive when they are used to fit
//                 120c, 105c, 90c, 80c, 70c aging experimental data.
//************************************************************************
#include <fstream.h>
#include <stdlib.h>
#include <ctype.h>
#include <iomanip.h>
#include <math.h>

const double start_MW = 500.0;      //the start MW of equilb. don't set as 0.0
const double end_MW = 100000.0;     //the end MW of equilb. you want to try

bool optimal(int, double [], double [], double&, double&, ofstream&);
double recusion(int, double [], double [], double, double&, double&, double&, double);
double square_diff(double, double, double, double, double);


int main(void){

        double days_of_aging[100]; //the array of the aging days
        double MW_of_aging[100];  //the array of measured MW for the each aging day
        int count_of_data;        //number of sets of experimental data
        double MW_E;   //MW_E is the first parameter in our model (equalibrium MW)
        double A;      //A is the second parameter in our model (sqrt(const*Kd*kh))
        char bump[10];

        ifstream inFile;            //inFile for input file
        ofstream outFile;            //outFile for output file
        char input[30];             //input file name
        int i;

        cout << "Please tell me the name of input file: ";
```

```
        cin >> input;
        cout << endl;

        inFile.open(input);
        outFile.open("output.dat");

        outFile.setf(ios::fixed, ios::floatfield);  //set up the output data format
        outFile.precision(6);
        outFile.setf(ios::left, ios::adjustfield);
        outFile << setw(15) << "MW_e" << setw(15) << "A" << setw(15) << "sd" << endl;


        inFile >> count_of_data; //get the sets of experimental data from input file
        cout << "It might take serveral minutes, cool down!\n" << endl;
        for(i=0; i<count_of_data; i++){
                inFile >> days_of_aging[i] >> MW_of_aging[i];
        }

        if(optimal(count_of_data, days_of_aging, MW_of_aging, MW_E, A, outFile)){
                cout <<"\nHit any letter(like Y) and enter to finish the program!\n";
        cin >> bump;
                cout << "Bye bye!" << endl;
        }
        else
                cout << "Exit program without getting a decent result!" << endl;

        inFile.close();             //close the input file
        outFile.close();            //close the output file
        return 0;

}



//************************************************************************
// subfunction: optimal()
// Function:        loop within the guessing MW_E range, and call recusion()
//                  to get the least square best fitting A for the given test_MW,
//                  and output the each sets of test_MW, test_A, SD,
//                  then get the least SD set of data,
//                  output the corresponding test_MW as MW_E, test_A as A.
// in:              count_of_data, sets of experimental data
//                  days_of_aging[], array of aging days
//                  MW_of_aging[], array of experimental MW for each aging days
//                  MW_E, MW of equlibrium
//                  A,  sqrt(const*Kd*kh)
//                  out, output file stream
// out:             MW_E, the optimal parameter after best fitting method
//                  A, the optimal parameter after best fitting method
//                  optimal(), return success or not
//************************************************************************
bool optimal(int count_of_data, double days_of_aging[], double MW_of_aging[],
                                        double& MW_E, double& A, ofstream& out){

        double accuracy=0.0001;       //set the accuracy you need
        double increment_MW=100.0;    //increment of the test_MW you want to try
```

```
    double test_MW, test_A;
    double start_guessA;     //the start value of guessing A
    double end_guessA;       //the end value of guessing A
    double sd, test_sd;      //least square standard deviation

    for(test_MW=start_MW; test_MW<=end_MW; test_MW=test_MW+increment_MW){
        start_guessA=0.0;     //set(reset) the start_guessA
        end_guessA=1.0;       //set(reset) the end_guessA

    //call subfunction recusion() to get the best fitting A for given test_Mw
        test_sd = recusion(count_of_data, days_of_aging, MW_of_aging,
                    test_MW, start_guessA, end_guessA, test_A, accuracy);
        out <<setw(15)<<test_MW<<setw(15)<<test_A<<setw(15)<<test_sd<< endl;

    //get the test_MW and test_A corresponding to the least test_sd
        if(test_MW==start_MW){
            MW_E=test_MW;
            A=test_A;
            sd=test_sd;
        }
        else{
            if(test_sd<sd)
            {
                MW_E=test_MW;
                A=test_A;
                sd=test_sd;
            }
        }
    }

    cout << "The final MW_E for our model is :" << MW_E << endl;
    cout << "The final A for our model is :" << A << endl;
    cout << "The least square deviation for the MW_E and A is :" << sd << endl;

    return 1;
}


double recusion(int count_of_data, double days_of_aging[], double MW_of_aging[],
    double test_MW, double& start_guessA, double& end_guessA,
        double& least_A, double accuracy){

    int i, k, leastK;
    double guessA;
    double incrementA=(end_guessA-start_guessA)/1000.0;
    double total_square_diff[1008];
    double least_sd;
    double rel_diff;


    for(k=1000; k>0; k--){
        guessA=start_guessA+incrementA*double(k);
        total_square_diff[k]=0.0;
        for(i=0; i<count_of_data; i++){
            total_square_diff[k]+=square_diff(MW_of_aging[0], days_of_aging[i],
```

```
MW_of_aging[i], test_MW, guessA);
                }
                total_square_diff[k]=sqrt(total_square_diff[k]/(count_of_data-1));
                if(k==1000){
                        least_sd=total_square_diff[k];
                        leastK=k;
                        least_A=guessA;
                }
                else{
                        if(total_square_diff[k]<least_sd){
                                least_sd=total_square_diff[k];
                                leastK=k;
                                least_A=guessA;
                        }
                }
        }


        if(leastK==1000)
                rel_diff=fabs((total_square_diff[leastK]-total_square_diff[leastK-1])/least_sd);
        else if(leastK==1)
                rel_diff=fabs((total_square_diff[leastK+1]-total_square_diff[leastK])/least_sd);
        else
                rel_diff=fabs((total_square_diff[leastK+1]-total_square_diff[leastK-
1])/least_sd);

        if(rel_diff<accuracy){
                return least_sd;
        }
        else{
                if(leastK==1000){
                        end_guessA=start_guessA+incrementA*(leastK);
                        start_guessA=start_guessA+incrementA*(leastK-1); }
        else if (leastK==1){
                        end_guessA=start_guessA+incrementA*(leastK+1);
                        start_guessA=start_guessA+incrementA*(leastK); }
        else{
                        end_guessA=start_guessA+incrementA*(leastK+1);
                        start_guessA=start_guessA+incrementA*(leastK-1); }

        return recusion(count_of_data, days_of_aging, MW_of_aging, test_MW,
                                        start_guessA, end_guessA, least_A, accuracy);
        }
}


double square_diff(double MW_ini, double aging_days, double exp_MW,
                                        double test_MW, double guessA){

        double diff;
        double B=(MW_ini*MW_ini+test_MW*test_MW)/(MW_ini*MW_ini-
test_MW*test_MW)
                        *exp(guessA*aging_days);
        diff=test_MW*sqrt(fabs((1.0+B)/(-1.0+B)));
        return (diff-exp_MW)*(diff-exp_MW);             }
```

```
//******************************************************************************
// Program: sec_simu.cpp
// Author:  Yao Lin
// Research Advisor: Dr. D. E. Kranbuehl
// Version: 0.99 beta
// Last Revised Date: 06/12/2000
// Project:        Based on conventional calibration plots got from the
//                 standard samples, use the concentration vs. retention volume
//                 slice data from the SEC-LS system to get the Mn, Mw, Mz and
//                 distribution information Mw/Mn, Mz/Mw.
// Comment:        Both the third order and first order calibration fitting plot
//                 have been used.
//******************************************************************************
#include <fstream.h>
#include <iomanip.h>
#include <stdlib.h>
#include <stdio.h>
#include <math.h>

double ev_to_mw_3rd(double);
double ev_to_mw_1st(double);

int main(){

  ifstream inFile;
  int i;
  long int count;
  double normal, t1, t2, t3, t4, MN, MW, MZ, Mw_over_Mn, Mz_over_Mw;
  char fileName[20];
  ofstream outFile;

  double conc[30000], ev[30000], mw[30000];

  cout << "Please input the file name of your table(elution time & conc.):" << endl;
  cin >> fileName;
  inFile.open(fileName);
  outFile.open("output.dat");

  count = 0;
  normal = 0;
  inFile >> ev[count] >> conc[count];
  do{
    normal += conc[count];
    count++;
    inFile >> ev[count] >> conc[count];
  }while(inFile);


  t1=0;
  t2=0;
  t3=0;
  t4=0;

  for(i=0; i<count; i++){
   mw[i] = ev_to_mw_3rd(ev[i]);
  }
```

```
 for(i=0; i<count; i++){
  t1+=conc[i]/normal;
  t2+=conc[i]/mw[i]/normal;
  t3+=conc[i]*mw[i]/normal;
  t4+=conc[i]*mw[i]*mw[i]/normal;
 }

 MN = t1/t2;
 MW = t3/t1;
 MZ = t4/t3;
 Mw_over_Mn = MW/MN;
 Mz_over_Mw = MZ/MW;

 outFile << "For the file: " << fileName << endl;
 outFile <<"By using third order polynomial calibration fit, we get: "
    << endl <<"MN = " << MN << endl << "MW = " << MW << endl
    << "MZ = " << MZ << endl << "MW/Mn = " << Mw_over_Mn
         << endl << "MZ/MW = " << Mz_over_Mw << endl << endl;


 t1=0;
 t2=0;
 t3=0;
 t4=0;

 for(i=0; i<count; i++){
  mw[i] = ev_to_mw_1st(ev[i]);
 }

 for(i=0; i<count; i++){
  t1+=conc[i]/normal;
  t2+=conc[i]/mw[i]/normal;
  t3+=conc[i]*mw[i]/normal;
  t4+=conc[i]*mw[i]*mw[i]/normal;
 }

 MN = t1/t2;
 MW = t3/t1;
 MZ = t4/t3;
 Mw_over_Mn = MW/MN;
 Mz_over_Mw = MZ/MW;

 outFile << "For the file: " << fileName << endl;
 outFile <<"By using first order polynomial calibration fit, we get: "
    << endl <<"MN = " << MN << endl << "MW = " << MW << endl
    << "MZ = " << MZ << endl << "MW/Mn = " << Mw_over_Mn
         << endl << "MZ/MW = " << Mz_over_Mw << endl << endl;

 inFile.close();
 outFile.close();

 return 0;

}
```

```
//third order calibration equation function
double ev_to_mw_3rd(double ev){

  double mw;
  mw = exp(80.115-9.8076*ev+0.474*ev*ev-0.00791*ev*ev*ev);
  return mw;

}


//first order calibration equation function
double ev_to_mw_1st(double ev){

  double mw;
  mw = exp(20.73874-0.5188*ev);
  return mw;

}
```

Vita

Born in Fuzhou, P. R. China, November 1, 1972. Graduated from No.1 Middle School of Fuzhou, July 1990. Earned a Bachelor of Science with a concentration in Polymer Science from the Fudan University, Shanghai, July 1995. Worked for Fujian Petro-chemical Ltd., China from Sep. 1995 to May 1998. Master of Arts candidate in Chemistry, the College of William and Mary, August 2000.

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