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Characterizing and monitoring changes in state of polymers during cure and use -aging

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CHARACTERIZING AND MONITORING CHANGES IN STATE OF POLYMERS DURING CURE AND USE-AGING

A Dissertation

Presented to
The Faculty of the Department of Applied Science
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Degree Requirements for the Degree of
Doctor of Philosophy

by
Andrew Orschel Meyer
2001
APPROVAL SHEET

This dissertation is submitted in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy

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Approved, March 2001

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Brian Holloway
David Thompson

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Abstract

Multi Angle Laser Light Scattering (MALLS) and Frequency Dependent Electromagnetic Sensing (FDEMS) provide unique characterizations of polymer systems during cure and use-aging. This research demonstrates that MALLS is the most accurate technique for absolute characterization of macromolecules, giving molecular weight and size information that other widely used and accepted techniques are incapable of measuring. Application of MALLS to monitoring the changing state of a polyamide-11 system in a water aging environment led to the discovery of an equilibrium molecular weight which is the result of two competing reactions, hydrolysis-degradation and a newly discovered recombination-polymerization reaction. The discovery of this recombination reaction creates the possibility of an indefinitely healthy polyamide-11 polymer system. FDEMS successfully monitored changing water content and degree of cure of a moisture-curing adhesive polymer. The data show potential for total in situ cure characterization by FDEMS, including in situ determinations of moisture diffusion rates during a polymer cure in the adhesive bondline.
CHARACTERIZING AND MONITORING
CHANGES IN STATE OF POLYMERS
DURING CURE AND USE-AGING
Chapter 1: Introduction

Frequency Dependent Electro Magnetic Sensing and Multi Angle Laser Light Scattering are proven techniques for molecular characterization. The challenge of these relatively new analytical techniques is assessing their applicability to a variety of material systems. Molecular weight measurements are vital to successful production of a wide variety of polymer materials, from wrinkle-free fabrics to high performance flexible tubing. Likewise, in situ characterization of material properties is invaluable for process and quality control of a wide range of materials, from coatings to ceramics.

Multi Angle Laser Light Scattering MALLS and Frequency Dependent Electromagnetic Sensing FDEMS have the potential to empower materials scientists to maximize material use lifetimes and increase efficiency and consistency of polymer cure by providing cutting edge detailed molecular information - absolute measurements of molecular weight and molecular size as well as in situ measurements of viscosity and degree of cure. Advances in absolute molecular weight characterization of polymers by MALLS and the development of FDEMS have initiated a departure from reliance on secondary techniques which are relatively time-consuming and not in situ or on-line.

Macroscopic performance properties such as tensile strength and elongation-yield characteristics for thermoplastics are directly related to molecular measurements and associated molecular properties such as average molecular weight — chain length and the molecular weight distribution. It has been shown that the molecular weight is
the principal microscopic property which governs the overall macroscopic performance properties of thermoplastics. Thus reproducible, accurate and absolute molecular weight characterization is necessary for understanding the changing state of an aging system and predicting remaining use life. And accurate, sensitive monitoring of polymer cure at the microscopic level using FDEMS is essential for understanding the changes occurring during cure and ensuring the intended performance properties.

Monitoring the process and aging of a material in a high performance environment is especially important when unexpected failure of the material gives rise to disastrous results. For an application such as offshore petroleum recovery or the adhesive bonding of materials the dangers are very real, and disaster prevention must be approached on two levels: identification / suppression of conditions which lead to failure, and the development of techniques to monitor the state of the material in situ during cure and use.

MALLS and FDEMS are among the most promising new technologies for materials characterization today: as will be discussed in Chapter 5. FDEMS is superior to other in situ techniques such as FTIR because of the convenience and versatility FDEMS affords. As shown in Chapters 3 and 4, MALLS is capable of total molecular characterization, providing information which is unobtainable by other characterization techniques such as solution viscosity, conventional Size Exclusion Chromatography, or even Right Angle Laser Light Scattering. One drawback is that MALLS necessitates that a [small] portion of the analyte be dissolved for measurement, thus the technique is not perfectly non-destructive. This problem can be sidestepped by sampling from non-essential portions of the use material or sampling
from a parallel and identical aging environment. The ultimate goal is to correlate molecular characteristics, measured by MALLS, to output from a perfectly non-destructive and *in situ* technique such as FDEMS.

It is the objective of this dissertation to demonstrate the ability of Multi Angle Laser Light Scattering to monitor on a molecular level the size and size distribution of polymeric materials and how they change with time during use. It is also the objective to show that Frequency Dependent Electromagnetic Sensing successfully monitors on the molecular level the changing state of a curing polymer system, over the range of unreacted prepolymer to the point of total cure. Together these two methods represent the latest advances in total macromolecular characterization.

The research is presented in four chapters:

• Chapter 2 is dedicated to discussing the two detection techniques, SEC-MALLS and FDEMS. These techniques have been applied in three investigations, each of which has involved extensive experimental work and all of which represent significant advances in macromolecular characterization. The next three chapters are articles describing these investigations which have been prepared for journal publication and are presented here as such. Specific details of the experimental approach to each investigation are included with each section.

• Chapter 3 explores characterization of the molecular weight of a new and rather difficult polymer system which was synthesized by the 3M Corp. The polymers for this study are of significant importance in 3M's recently changing water repellant division, and the complexity of this particular polymer system provides an excellent
opportunity to test the validity of two leading polymer laser light scattering
characterization techniques. Molecular characterization by light scattering is rapidly
becoming the standard not only for polymer characterization but also within
biotechnology research. This Chapter presents a strong case for the validity of Multi
Angle Laser Light Scattering as well as convincing results which call into question the
applicability of Right Angle Light Scattering to unknown polymer systems.

- Chapter 4 discusses monitoring aging in Polyamide-11 (PA-11) used for
  offshore recovery efforts by the petroleum industry. Accurate measurement of
  molecular weight is essential in predicting use life in these high-risk, high-
  performance environments. Using the MALLS characterization technique verified in
  the previous chapter, a revealing aging study on changes in PA-11 molecular weight
  with time in a water environment shows that previous theories on the aging profile of
  PA-11 are incomplete. that in fact an equilibrium molecular weight is reached and that
  there is a competing recombination reaction during aging.

- Chapter 5 focuses on measurements of dielectric properties using FDEMS to
  monitor cure in a moisture-curing isocyanate system. Moisture is an important
  parameter in the cure of this system as well as during its use, and there are no other
  techniques capable of measuring water content or extent of cure both continuously and
  in situ in this polymer system. Ultimately FDEMS could be used for in situ
  monitoring of cure and changes in state of a number of polymeric systems, including
  the PA-11 system.
References for Chapter 1


CHAPTER 2: EXPERIMENTAL METHODS

Size Exclusion Chromatography

Size Exclusion Chromatography (SEC) is another secondary method for determining polymer molecular weight in solution. This technique, also known as gel permeation chromatography (GPC), was first demonstrated as early as 1959 for aqueous applications. The physical basis of SEC/GPC is separation by molecular size. This technique, as opposed to other types of chromatography, is steric-based and thus involves no chemical interaction between the analytes and separating column. Depending on the hydrodynamic volume of a solute molecule in solution, solvated particles passing through a soft, porous gel packing penetrate the pores to varying degrees. Particles with relatively small hydrodynamic radii are retained longer by the gel, while larger particles are excluded from the gel packing and elute sooner.
Typical methods of detection for conventional SEC include in-line refractive index measurements, in-line viscosity, and UV absorption. Using data from known standards, a calibration plot of molecular weight and retention volume can be constructed and used to calculate the weight average and number average molecular weights of a polymer as well as determining the weight distribution of the sample. This approach is known as the conventional calibration approach and requires that the polymer for analysis be either the same type of polymer as that used for construction of the calibration curve, or a polymer with the same hydrodynamic volume/molecular weight ratio as the standards.

Figure 5 is a typical elution curve, showing schematically the void volume $v_0$ of total exclusion and the useful range of molecular sizes and elution volumes for a typical column.
A universal calibration curve has been proposed. This approach compensates for varying degrees of swelling in solution which give rise to a departure from a conventional calibration curve. The universal calibration curve includes a measured intrinsic viscosity, and it is constructed using refractive index data and viscosity data. This approach assumes that the product of viscosity $\eta$ times molecular weight $M$ is directly related to the hydrodynamic volume in the same way for all polymer systems. The working assumption necessary for applicability of the universal calibration is that neither the nature of the solvent nor that of the polymer gives rise to a departure from the universal calibration curve for a given chromatography system. Nevertheless, a calculation of molecular weight, $M$, based on either retention volume or viscosity...
alone is necessary to construct the universal calibration curve, thus the approach is subject to sources of error inherent in a secondary technique.

Problems with the SEC method include the need for frequent calibration to account for column shifting and the simple fact that the method is a secondary approach. For certain polymer systems such as PA-11, known standards are not available or the viscosity-molecular weight results do not fall on the universal calibration curve. Absolute techniques are necessary for accurate analysis in these cases.
Multi Angle Laser Light Scattering

Multi Angle Laser Light Scattering, MALLS, provides absolute molecular weight characterization of macromolecules. MALLS proves to be of great historical significance in the field of macromolecular characterization because recent developments have made the technique relatively simple and it requires no calibration by known standards.² The use of MALLS in concert with Size Exclusion Chromatography SEC allows for total molecular characterization of not only the weight average molecular weight of a polymer sample, but also a measure of the molecular weight distribution – including calculated values for number average molecular weight, Mₙ, and the z-average molecular weight, Mₓ. Finally, MALLS also provides insight to molecular size and a measured root mean square radius, <r²>, for macromolecules in solution.²⁻¹¹

Light scattering can be observed in many naturally occurring phenomena, including the blue color of the sky, a red sunset, or diffuse automobile headlight beams through a fog. MALLS fundamentals are derived from the findings of Lord Rayleigh in 1871.¹² The root physical principle behind light scattering is the fact that when light strikes an atom or molecule the electrons of the atom or molecule are displaced from their equilibrium position, giving rise to an induced dipole. Given the oscillating electric field in which light travels, E, which causes motion of an electron of charge -e, over a distance X, we see an induced dipole moment μ.:¹³
\[ \mu = -eX \quad (2.1) \]

and

\[ \mu = \alpha E \quad (2.2) \]

where \( \alpha \) is the polarizability of the electron. Combining equations (2.4) and (2.5) and rearranging:

\[ X = -\frac{\alpha E}{e} \quad (2.3) \]

Thus the displacement of the electron is directly related to its polarizability and the field strength of the incident beam of light.

Rayleigh studied light scattering of molecules in the gas phase.\(^{12}\) He demonstrated that light scattering was related to the molar mass of the scattering particle, \( M \), its concentration, \( c \), its specific refractive index increment, \( \frac{dn}{dc} \), Avogadro's number, \( N_A \), the scattering angle \( \theta \), and the wavelength of the incident beam, \( \lambda \), as\(^{12}\)

\[ R_\theta = \left( \frac{2\pi^2}{N_A \lambda^4} \right) \left( \frac{dn}{dc} \right)^2 \left( 1 + \cos^2 \theta \right) Mc \quad (2.4) \]

This quantity, \( R_\theta \), is known as the Rayleigh ratio for the intensity of scattered light.

For particles in solution equation (2.7) was shown by Debye to become:\(^{12}\)

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where $K^*$ is a constant which includes $dn/dc$, $\lambda$, and the refractive index of the solvent. $M_w$ is the weight average molecular weight. $A_2$ is the second virial coefficient, a measure of solvent-polymer interaction. $R_\theta$ is measured, and $P_0$ is the scattering function - a measure of the angular variation of scattered light. Using this equation for extrapolating $<r_g^2>$ and the quantities $A_2$ and $M_w$ is a formalism proposed by Bruno Zimm.\textsuperscript{12}

**Figure 6**

![Graphical representation of the equation](image)
Figure 6 is a typical Zimm plot showing the double extrapolation technique, where empty circles are measured points and filled squares are extrapolated points. Here double extrapolation to zero angle and zero concentration yields $M_w$. Extrapolation to zero concentration corrects for scattering interference between molecules, and extrapolation to zero angle mathematically eliminates the angular effect on the scatter for calculation of $M_w$. Both of these conditions, zero concentration and infinite dilution, are impossible to achieve experimentally, but each can be approximated well via a series of measurements at multiple concentrations and multiple angles.

Because the concentration is extremely small when measuring inline with dilute solutions injected into a chromatography system, the $2A_2c$ term can be neglected in equation (2.6). This estimation is reasonable and allows for measurement with only one solution concentration.

Light scattering is an extremely powerful technique for calculating molecular weight because of its accuracy and ease of use. The factors in equation (2.6) are all known or directly measured quantities, leading to an absolute measurement of $M_w$. This accuracy provides far more reliable data than secondary techniques such as solution viscosity or calibrated SEC.

Nevertheless, SEC proves to be useful when used in concert with MALLS. Separation of the sample by size provides the opportunity to make a series of $M_n$ determinations for size-separated components of a polymer sample incrementally rather than a single light scattering measurement for the sample in its entirety. Using MALLS with SEC provides data which shows the relative amounts of polymer over
the molecular weight range of the sample, a statistical $M_n$, a statistical $M_z$, and the same weight average molecular weight which would be obtained without SEC.\textsuperscript{14}

In addition to molecular weight data, MALLS also provides information about molecular size and shape, using knowledge of relationships between molecular size and mass. For example, the slope obtained by plotting the log $<r_g^2>$ vs. log $M_w$ can be used to determine molecular conformation.\textsuperscript{15}

The root mean square radius $<r_g^2>$ is calculated directly from the light scattering angular $P_\theta$ data. Unlike other methods for measuring molecular size, this calculation requires no assumptions of molecular shape or conformation. Rather, it uses measurements of light scattering intensity over a series of known scattering angles to elucidate molecular size. The calculation is based on the theory that scattered light will interfere destructively depending on pathlength through a given polymer molecule. The amount of interference is related to the size of the polymer chain and the angle of scatter. Quantitatively, $P_\theta$ is related to $<r_g^2>$, $\theta$, and $\lambda$ as\textsuperscript{12}

\[
\frac{1}{P_\theta} = 1 + \left( \frac{16\Pi^2}{3\lambda^2} \right) <r_g^2> \sin^2(\theta/2) \quad (2.6)
\]

Solution viscosity can be used to measure the hydrodynamic radius of a polymer in solution, but this is a secondary technique which requires an assumption of chain conformation-shape in solution to calculate accurate radius values. Thus light scattering is a far more reliable method for measuring polymer radius in solution. Measurement of $<r_g^2>$ does have its limits within light scattering, however. Meaningful $<r_g^2>$ values cannot be obtained if the radius is less than $\lambda/20$ because the
change in pathlength through such small molecules is not sufficient to cause a significant amount of destructive interference. In this case the molecule scatters in all directions equally. Molecules with radii on the order of \( \lambda \) or larger give rise to resonance peaks, as the interference of scattered light can be out of phase by whole cycles, giving rise to both constructive and destructive interference.

**Figure 7**
Schematic: Angular Dependence of Light Scattering

![Diagram showing angular dependence of light scattering.](image)
Development of a Room Temperature SEC-MALLS System for Difficult to Dissolve Polar Polymers

For absolute molecular weight characterization of the polymer systems described in Chapters 3 and 4, a room-temperature SEC-MALLS system was developed (Figure 8). This project was completed in two stages: development of a room temperature SEC system, followed by the addition of MALLS detection.

The SEC system used RI detection by a Viscotek Model 200 Differential Refractometer and a conventional calibration curve based on elution volumes of known standards to calculate molecular weight. The most important step in the development of this system was finding a suitable mobile phase and chromatography column for the hard to dissolve PA-11 system. The only known room temperature solvents for PA-11 are 1,1,1,3,3,3 hexafluoroisopropanol (HFIP) and m-cresol. both of which require extremely careful handling and use. The choice of HFIP as the mobile phase was based on the high viscosity of m-cresol at ambient temperature. ~20.8cp. as compared with that of HFIP. ~1cp.\textsuperscript{17} For SEC-HPLC applications the mobile phase must be of a low viscosity in order to prevent excessive backpressure which will crush the column gel.

Two types of SEC column were considered: a Polymer Laboratories, Inc. PLGel PS/DVB column, and a Jordi Associates JordiGel DVB column. The PLGel column was determined to be unsuitable for use with HFIP because of excessive gel swelling which resulted in high column backpressure. Thus the JordiGel DVB column was selected and implemented into the SEC system with column heating at 40°C to
further reduce backpressure. Drift in the RI signal was minimized by including molecular sieves in the mobile phase source. These sieves trap and remove moisture and other impurities from the HFIP.

**Figure 8**
Schematic of SEC-MALLS System

A Waters 515 HPLC pump was chosen to provide the constant 0.6mL/min flow of mobile phase through the SEC system. Typical seals for the pump heads were destroyed by the unique use conditions of this SEC system. Low pressure PTFE seals were inadequate for the 600psi operating pressure. High pressure seals made from a proprietary material were provided; these seals though chemically resistant to many commonly used organic mobile phases such as THF or chloroform, dissolved in the HFIP mobile phase in a matter of minutes. A third set of seals, also made from a
proprietary material. was provided which withstood both the pressure and the strong solvent nature of the HFIP mobile phase.

Mobile phase filtration was implemented at several points in the system. HFIP was first drawn into the pump through a 2µm steel filter attached to the end of the solvent inflow tubing and an additional 2µm inlet filter in the pump itself. A 0.5µm inline filter frit after the injector was installed to prevent impurities in sample injections from clogging the chromatography column. A DVB guard column with 2µm inlet and outlet frits was installed as a final protective unit before the chromatography column.

The conventional calibration used in the SEC system was based on PMMA standards, which only approximately match the mass to size ratio of PA-11 and other polymer systems. Other common polymeric standards, e.g. PS, are not soluble in HFIP.17 and narrow standards of PA-11 are not possible to synthesize because PA-11 is polymerized via a condensation polymerization.

After months of use it was determined that additional detection by light scattering would greatly enhance the information obtained in the SEC system. Two systems were considered: a Precision Detectors PD 2000 Low Angle Laser Light Scattering, LALLS, detector, and a Wyatt miniDawn MALLS detector. Preliminary testing with the PD instrument demonstrated that the two-angle (15° and 90°) detection system was able to detect polymer eluting from the SEC system, but the signal-to-noise ratio was not acceptable, particularly for the low angle 15° detector. Thus only one detector, 90°, was providing useful data for our SEC system.
The Wyatt miniDawn MALLS detector included three light scattering detectors. 45°, 90° and 135°, and gave a much higher signal-to-noise ratio for all three detectors. In addition, MALLS is capable of calculating the root mean square radius while LALLS cannot.\textsuperscript{18} The Optilab 903 RI detector was installed with the miniDawn, using filtered monochromatic light at the same wavelength as the miniDawn, 690nm, and proved to be a more sensitive differential refractometer than the Viscotek Model 200. The Optilab refractometer signal was drifting with slight temperature changes, which required room-temperature equilibration via a water pump and a heat sink in order to achieve a stable baseline.

Finally, installation of a column selector allowed for bypass of the chromatography column for rapid data collection without separation. This technique, known as Rapid Multi Angle Light Scattering, has been shown to provide accurate and reproducible measurement of Mw in a fraction of the time for full characterization by SEC-MALLS.\textsuperscript{19}

After successful attainment of a stable RI baseline, the miniDawn was able to successfully obtain MALLS measurements of the separated polymers eluting from the SEC system. However, installation of replacement chromatography columns introduced new noise into the LS baseline while the RI baseline remained stable. It was suggested by Dr. Howard Jordi that particulates would exit a new column for a time after installation and that these particulates were not seen at initial installation of the MALLS detector because the chromatography system had been in use prior to that time.\textsuperscript{20} In attempting to remove these fine particulates, or “fines,” it was discovered that repeated purging with m-cresol injections onto the DVB column would effectively
remove the fines. Otherwise the process of flushing the columns with low viscosity mobile phase would require an excessive amount of time.

Recapture of mobile phase is made possible by recycling the outflow of the system back into the mobile phase source for an offline system, and capturing and distilling mobile phase after use with dissolved polymer. The distillation requires extreme care and attention to ensure that the proper distillation temperature 58°-59°C is maintained and that the HFIP is kept tightly sealed to prevent loss by evaporation and to minimize health risks.

This high performance polymer characterization system requires constant attention due to its inherent vulnerability to changes in temperature, mobile phase chemistry, or regular failure of working parts which will disrupt the baseline signal. Nevertheless, the system is unique in its ability to provide absolute molecular weight characterization of hard to dissolve polymer systems.
Frequency Dependent Electromagnetic Sensing

Frequency Dependent Electromagnetic Sensing (FDEMS) is a versatile, convenient and non-destructive method for measuring microscopic changes in a reactive chemical system such as a polymerization reaction. The FDEMS technique utilizes impedance measurements taken at frequencies in the Hertz to Megahertz range, monitoring the motions of dipoles and ions in the dielectric medium in order to track changes in molecular properties. FDEMS monitors these changes continuously and in situ, i.e. the sensing probe collects data from within the reactive medium itself as the reaction progresses.

At the heart of this technique is the response of dipoles and ions to an applied electric field. An electrical force induces charged species to move within the reactive medium, and FDEMS monitors changes in these movements, rotational, translational and otherwise, over a broad spectrum of frequencies and throughout the reaction. FDEMS monitoring has been shown to be useful over periods from a few seconds (rapid cure) to numbers of years (life monitoring) in order to correlate molecular changes to the closely associated macroscopic variations seen in the bulk.

Polarization

An exploration of the electrical nature of atoms and molecules is necessary in order to understand the working force behind dielectric measurements. FDEMS takes advantage of the translational and rotational movement of the electrical charge in atoms or molecules as ions or dipoles when exposed to an external electric field. Such behavior is observed on a variety of levels under an applied field, $E_a$. 

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• Ionic motion within the reactive medium. Ions attracted toward oppositely charged plates.
• Rotation of permanent dipoles within the medium. Molecules rotate to respond to the force of the electric field, \( E_a \).
• Induction of dipoles in molecules with otherwise symmetrical charge arrangement. Electron clouds in atoms or whole atoms within molecules are distorted from their normal positions in response to \( E_a \).

Changes of a polar nature can be defined by the sum of the distortion polarization and the dipolar orientation polarization, giving the total polarization, or total molecular polarization response to \( E_a \).\(^{22}\)

\[
P_{\text{total}} = P_{\text{distortion}} + P_{\text{dipolar}} \quad (2.7)
\]

The response of a given molecule to \( E_a \) is termed the polarizability of the molecule, \( \alpha \). In turn, the average total polarized dipole moment of a molecule, \( \mu_t \), is defined as the multiple of the applied force, \( F \), and the polarizability, \( \alpha_t \).\(^{22}\)

\[
\mu_t = \alpha_t F \quad (2.8)
\]

Thus the total polarization \( P_{\text{total}} \) is the product of the number of molecules, \( N \), their polarizability, \( \alpha_t \), and the applied force, \( F \):
The magnitude of the various components of \( P_{\text{total}} \) is determined by the frequency of \( E_a \). For example, in the frequency range of \( 10^2 \) to \( 10^7 \) Hz, dipolar absorption is at a peak. In this frequency range the movements of molecular dipoles are sufficiently fast to move along the same time scale as the alternating \( E_a \). Below this frequency range we see absorption due to interfacial polarization, an effect involving the buildup of charges at interfaces between phases in the polymeric material. At frequencies above the dipolar range, the absorbance is the result of changes on the atomic level. Dipolar movements can no longer align with the changing \( E_a \), but distortions of atomic nuclei and at even higher frequencies distortions of electron clouds result in absorbance peaks.

FDEMS effectively utilizes the dipolar region of absorbance wherein the atomic and electronic distortions occur instantaneously. This selectivity allows for accurate measurement of \( P_{\text{dipolar}} \) separately as a component of \( P_{\text{total}} \)\(^{22}\)

\[
P_{\text{dipolar}} = N\alpha_{\text{dipolar}} F \quad (2.10)
\]

**Capacitance**

In order to fully understand the method of measuring dielectric properties via impedance measurements as described above, we consider a macroscopic model of capacitance. Figure 9 below depicts a classic parallel plate capacitor with a potential.
V. across the plates resulting in charges $Q^+$ and $Q^-$ on the plates, per unit area. The capacitance of the plates is defined as

$$C = \frac{Q}{V} \quad (2.11)$$

As pictured in Figure 9, a dielectric will be polarized in the electric field, resulting in a new capacitance:

$$C' = \frac{(Q+P)}{V} \quad (2.12)$$

where $P$ is the polarization of the dielectric.$^{24}$

Figure 9: Dipole Orientation$^{25}$
Some assumptions are required to move further. First we assume that the electric field in our capacitor is perfectly uniform. This assumption allows the voltage - $V$ to be expressed as a function of the electric field and the plate separation, $s$. or

$$V = E_s s \quad (2.13)$$

Our next assumption is that the field at any discrete point between the plates but not near the edges is equivalent to the field between two infinitely large planes of charge $Q$. This is a reasonable assumption for FDEMS because particle size is insignificant compared to the size of the sensing leads on an FDEMS sensor. We know (Gauss's Law) that $E$ for an infinite plane of charge is

$$E = \frac{\sigma_s}{2\varepsilon_o} \quad (2.14)$$
where $\varepsilon_0$ is the permeability of free space, 8.85 pF/m, and $\sigma$ is the charge – Q per unit area – A on a single plate:

$$\sigma_s = \frac{Q}{A} \quad (2.15)$$

Substituting equations (2.14) and (2.15) into equation (2.13) for two planes of charge we get

$$V = \frac{(\sigma_s/2\varepsilon_0)s}{(Q/\varepsilon_0A)s} \quad (2.16)$$

Simplifying equation (2.16) with equation (2.11) yields:

$$C = \frac{\varepsilon_0A}{s} \quad (2.17)$$

Thus we see that capacitance is exclusively dependent upon geometry; that is, the FDEMS sensors must be consistent and precise.

**Permittivity**

As stated earlier FDEMS utilizes impedance measurements. From impedance at a given frequency it is possible to calculate the capacitance, $C$, and the conductance, $G$, of the dielectric. Impedance, $Z$, is related to capacitance and conductance by

$$Z^{-1} = G + i\omega C \quad (2.18)$$
where $\omega = 2\pi f$. FDEMS calculates the components of the complex permittivity, $\varepsilon^\ast$, from the impedance measurements. The components of $\varepsilon^\ast$ are the dielectric permittivity, $\varepsilon'$, and the dielectric loss factor, $\varepsilon''$:

$$\varepsilon^\ast = \varepsilon' - i\varepsilon'' \quad (2.19)$$

Electric current in phase and out of phase with the voltage can be defined as

$$I = i\omega C_0\varepsilon^\ast V = (i\omega C_0\varepsilon' + \omega C_0\varepsilon'')V \quad (2.20)$$

Substitution with Ohm's law and equation (2.18) gives

$$Z^{-1} = i\omega C_0\varepsilon' + \omega C_0\varepsilon'' \quad (2.21)$$

Finally, replacing the $Z^{-1}$ term with equation (2.18) yields

$$G + i\omega C = i\omega C_0\varepsilon' + \omega C_0\varepsilon'' \quad (2.22)$$

Which allows us to form equations (2.23) and (2.24) for calculating the dielectric permittivity, $\varepsilon'$, and the dielectric loss factor, $\varepsilon''$:

$$\varepsilon' = C/C_0 \quad (2.23) \quad \text{and} \quad \varepsilon'' = G/\omega C_0 \quad (2.24)$$
Both $\varepsilon'$ and $\varepsilon''$ have ionic, dipolar and inducted electronic components. However, at the measurement frequencies used by FDEMS the electronic components are small. Their response is much faster and is represented by $\varepsilon_{\infty}$, a constant. Therefore $\varepsilon'$ and $\varepsilon''$ are best represented by

\[ \varepsilon'_{\text{total}} = \varepsilon'_{i} + \varepsilon'_{d} + \varepsilon_{\infty} \quad \text{and} \quad \varepsilon''_{\text{total}} = \varepsilon''_{i} + \varepsilon''_{d} \quad (2.25) \]

Depending on the conditions of a system monitored by FDEMS, either the ionic or the dipolar component can dominate. In a viscous, low temperature medium at high frequency the translation of ions is limited, giving rise to only a small ionic contribution but a relatively large response by dipolar rotations. Conversely, a system at higher temperature with a lower viscosity and a lower frequency will show a much larger ionic contribution which will dwarf the response by dipolar rotations.

The complete equations using the Debye model for dipolar rotation and for the ionic portion of $\varepsilon'$ and $\varepsilon''$ are as follows:\textsuperscript{30}

\[ \varepsilon' = \varepsilon_{\infty} + (\sigma_{0} - \varepsilon_{\infty})/ (1 + \omega^{2}\tau^{2}) \quad (2.26) \]

\[ \varepsilon'' = (\sigma / \omega \varepsilon_{0}) + [ (\varepsilon_{0} - \varepsilon_{\infty}) \omega^{2}\tau ] / (1 + \omega^{2}\tau^{2}) \quad (2.27) \]

**Ionic Conductivity**

The first term in equation (2.19) is the portion of the ionic character due to conductance of ions, and the symbol $\sigma$ is the conductivity of the dielectric. Its units
are ohm\(^{-1}\)cm\(^{-1}\). Clearly at low frequencies when the dipole polarization effect is absent, the conductivity can be expressed as:

\[ \sigma = \varepsilon_o \omega \varepsilon'' \quad (2.27) \]

**The Debye Equations**

An important aspect of dielectric measurements is the fact that the ionic, dipolar and electric fluctuations all take time. Each of these effects will respond differently depending on the frequency of the applied electric field. For example as mentioned earlier, at the typical use frequency for FDEMS electric fluctuations reach a maximum instantly. Dipolar rotations, however, take much longer to equilibrate to the change in \(E_a\).

At a certain frequency the dipolar fluctuations will no longer be able to equilibrate fully with the changing electric field, leading to dielectric relaxation.

The Debye expressions for \(\varepsilon'\) and \(\varepsilon''\) are as follows:

\[ \varepsilon' = n^2 + \frac{(\varepsilon_o - n^2)}{(1 + \omega^2 \tau^2)} \quad (2.28) \]

and

\[ \varepsilon'' = \frac{[ (\varepsilon_o - n^2) \omega \tau ]}{(1 + \omega^2 \tau^2)} \quad (2.29) \]

where \(\tau\) is the relaxation time. It represents an average time for rotational relaxation motion of the dipoles.
Figures 11a and b plot equations (2.28) and (2.29) vs. log(ωτ) respectively.\textsuperscript{32}

**Figure 11: Debye Expressions**

These plots illustrate that for an ideal dielectric material a dipolar relaxation absorption occurs at a particular frequency for $\varepsilon'$ and $\varepsilon''$. The relaxation time $\tau$ equals $\omega^{-1}$ when the value of $\varepsilon''$ is at its maximum. The relaxation time $\tau$ is a quantity directly related to the glass transition temperature and the viscosity of a polymeric system.\textsuperscript{33,34} To better understand the physical nature of relaxation we consider Figure
9. a polarized dipolar state. If the $E_a$ is turned off the dipoles will slowly return to a random configuration. This process is known as relaxation. A similar state is reached if the frequency of $E_a$ is too fast for dipolar movement to keep up. In this case the dipoles will again approach a random orientation because the effect of $E_a$ is only to slightly "shake" the dipoles back and forth, at most, with no effect at all if the frequency is far too high.

In a polymerizing system the viscosity will increase as the reaction progresses. It is possible to monitor a polymerization via FDEMS at a given frequency or a discrete set of frequencies by monitoring the change in $\varepsilon'$ and $\varepsilon''$. As the viscosity of the system rises the response of $\varepsilon''$ at each frequency will change and eventually reach a relaxation point where $\tau$ at that point equals $(2\pi f)^{-1}$. Thus FDEMS is extremely effective for monitoring the changing glass transition temperature and degree of cure for a polymer system as the changes affect the relaxation time, $\tau$. 

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References for Chapter 2


Chapter 3:

Multi Angle Laser Light Scattering Analysis of a Poly (Fluoro Acrylate)

The following article describes the detailed molecular analysis of a poly (fluoro acrylate), PFA, a polymer which has been developed and synthesized by the 3M Corporation for potential use by 3M’s water repellants division. The article examines two currently very widely used macromolecular characterization systems: Multi Angle Laser Light Scattering (MALLS) and Viscosity–Right Angle Laser Light Scattering (RALLS). The viscosity-RALLS system, manufactured by Viscotek Corp., is employed by roughly half of all analytical macromolecular characterization laboratories today and employs an in-line Triple Detector SEC™ System, including a four-capillary differential viscometer, the Right Angle Laser Light Scattering detector and a differential refractometer. The Multi Angle Laser Light Scattering technique has been championed by Wyatt Technology Corp., and employs a three-angle or a seventeen-angle laser light scattering detector with a differential refractometer.

In the context of Chapter 3 and the characterization of PFA analysis, the methodology of each detection system is explored, including a look at the measurement and determination of PFA weight-average molecular weight, Mw, and PFA mean square radius of gyration, \( <r_g^2> \). Significant differences in the results obtained for the set of PFA polymers by the two systems are explained by the
fundamental differences in assumptions, equations and detectors each system uses to calculate its Mw and $\langle r_g^2 \rangle$ results. There is a major difference in that assumptions about molecular conformation and semi-empirical formalisms are required by the viscosity-RALLS system, and that no such assumptions or empirical equations are necessary when using MALLS. MALLS is an absolute technique. It is known that the RALLS assumptions, i.e. the necessary estimate of the Mark-Houwink constant, the Flory-Fox and Ptitsyn-Eizner formalisms, are valid for many well-known and well-characterized macromolecules, hence the wide use and acceptance of the viscosity-RALLS technique. However, with the continuing development of new polymers which are complicated in structure with unknown characteristics and especially with the advent of biotechnology / protein characterization, absolute characterization of macromolecules is extremely important, and the accuracy of viscosity-RALLS technology needs to be re-evaluated.

A team of synthetic chemists at 3M in St. Paul, MN. successfully polymerized a sample set of this PFA polymer using two polymerization techniques:

- One group of samples was polymerized in a fluorinated organic phase using 2.2'-Azobisisobutyronitrile (AIBN) as the initiator and dodecylmercaptan (DDM) as a chain transfer agent. The amount of initiator and chain transfer agent used in the synthesis was varied over this group in order to generate polymers with varying molecular weights and performance characteristics, and to begin the process of optimizing the polymerization reaction with respect to
reaction time, use of costly materials (e.g. monomer, initiator, and transfer agents) and overall success of the synthesis.

• Another PFA polymer was synthesized using a water emulsion polymerization technique with a cosolvent of acetone. The initiator was a Vazo VA050 initiator, and a cationic surfactant was also used in the mixture. Only one large Mw sample from this polymerization technique was of interest.

Typically, characterization of new polymers by Size Exclusion Chromatography and Laser Light Scattering is performed by 3M at their own analytical laboratory using conventional techniques. PFA has unique performance properties as a fluorinated, repellant material. However it is not soluble in solvents which are commonly used for SEC-LLS polymer characterization, such as water, tetrahydrofuran and chloroform, and thus the 3M analytical lab could not characterize it. The only known solvent for this polymer thus far is hexafluoroisopropanol, HFIP. 3M’s analytical lab does not have a SEC-LLS system running with HFIP mobile phase, so the sample characterization had to be outsourced.

The 3M analytical laboratory first sent batches of these PFA polymers to the Viscotek Corporation for analysis in Viscotek’s “Triple Detector” system. The results from this system were not what the analysts at 3M had expected, and the samples were sent for absolute molecular weight analysis by Multi Angle Laser Light Scattering.
Wyatt Technology had no MALLS system in use with HFIP as the mobile phase, thus the samples were sent to William & Mary for analysis.

The initial $M_w$ and $R_g$ MALLS results were significantly larger than those from the viscosity-RALLS system. This difference was believed to be the result of different SEC operating conditions, namely that the viscosity-RALLS system used HFIP mobile phase with an organic salt but the MALLS system used HFIP with no salt. To verify this hypothesis a second MALLS trial was performed at William & Mary using organic salt in the HFIP mobile phase to evaluate this assumption. The $M_w$ and $<r_g^2>$ values were the same in this second trial as in the testing without salt.

The article explains in detail why the MALLS results are absolute and reliable, and shows that the viscosity-RALLS approach does not work, giving the wrong results. These results will have a significant impact on the future direction of macromolecular characterization as they point out that viscosity-RALLS cannot be relied on for characterization of a complex polymeric system. In addition, this study confirms the choice of using MALLS detection for the characterization of other hard to dissolve polymer systems such as polyamides. The measurements by MALLS are absolute and require no need for changes in assumptions as the polymer changes throughout its lifetime, and thus can be used to monitor changes in state during use-aging.
Abstract. Two leading macromolecular characterization techniques were employed for analysis of a unique, difficult to dissolve fluorinated polymer system (PFA). Poly(N-methyl perfluoroctyl sulfonamido ethyl acrylate). Multi Angle Laser Light Scattering (MALLS) and Viscosity – Right Angle Laser Light Scattering (RALLS) were used to measure the weight average molecular weight and molecular size-radius using the solvent HFIP, 1.1.1.3.3.3 – hexafluoroisopropanol. HFIP is shown to be an excellent solvent for light scattering measurements on the PFA as well as on Polyamide-11 and Polymethyl methacrylate. It is shown that the Viscosity-RALLS approach is not a valid technique for the PFA polymer system due to the assumptions used.
Introduction

A unique series of poly (fluoro acrylates) were synthesized and characterized using laser light scattering techniques. The polymers, referred to as PFA, are of potential industrial importance as water repellants and were synthesized and characterized for the first time in this study. Development and use of techniques to measure molecular size and conformation in solution remains an essential but often difficult step in characterizing new polymer systems. The appropriate choice and implementation of solvent, measurement technique and test conditions is a challenging task, given the lack of information available when characterizing a new polymer for the first time.

The objective of this study is to identify the molecular weight, the molecular weight distribution and the conformational behavior of this PFA polymer in solution. Techniques used are size exclusion chromatography with viscosity and two different laser light scattering detectors. The results are compared to those from other polymer systems. In addition, the role of an additive salt to electrically balance the solvated polymer and potentially reduce solvent chain expansion behavior of the polymer in solution is examined.
Experimental

The poly (fluoro acrylates) were polymerized and provided by the 3M Corp.

Figure 1 displays the chemical structure of the monomer unit:

![Figure 1: PFA monomer Unit](image)

The polymerization chemistry was carefully controlled and designed to produce a set of samples of varying molecular weights. The level of initiator was kept constant for samples 1 through 5, and a decreasing amount of chain transfer agent was used for each sample in the set, with sample 1 having the most chain transfer agent and sample 5 having none. Samples 6 and 8 were polymerized with varying amounts of initiator and no chain transfer agent. Sample 9 was polymerized using an emulsion polymerization and no chain transfer agent.
Table I: PFA Polymerization Chemistry Matrix

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chain Transfer Agent, Weight %</th>
<th>Initiator, Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.65%</td>
<td>0.20%</td>
</tr>
<tr>
<td>2</td>
<td>0.83%</td>
<td>0.20%</td>
</tr>
<tr>
<td>3</td>
<td>0.50%</td>
<td>0.20%</td>
</tr>
<tr>
<td>4</td>
<td>0.21%</td>
<td>0.20%</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0.20%</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0.10%</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0.25%</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0.20%</td>
</tr>
</tbody>
</table>

Because the fluoro acrylates are not soluble in most conventional solvents but are soluble in hexafluoroisopropanol, HFIP. background studies were carried out on two types of polyamide-11, PA-11, and on poly(methylmethacrylate), PMMA, standards to verify the compatibility of the HFIP-SEC macromolecular characterization technique. These include commercial samples of Atochem’s Besno P40TL, a plasticized PA-11, extruded into pipe. In addition unplasticized PA-11 made in our laboratory by polymerization of 11-aminoundecanioic acid was characterized. Four samples of varying molecular weight were made. These samples were made in an oven flushed with Argon gas and held at 190°C and under a reduced pressure of 380 torr. In order to control the molecular weight, reaction times were varied: 12 hours for two high molecular weight samples ($M_w \approx 78.000$ & $72.000$) and 1.5 and 0.75 hours for lower molecular weight samples ($M_w \approx 30.000$ & $14.000$), where $M_w$ is the weight-average molecular weight. PMMA narrow molecular weight standards were purchased from Polymer Laboratories, Inc.
Multi Angle Laser Light Scattering

Size exclusion chromatography (SEC) was conducted with 1.1.1.3.3.3-hexafluoroisopropanol as the mobile phase at a flow rate of 0.6mL/min with a JordiGel DVB Mixed Bed HPLC column at 40°C. To obtain absolute measurements of weight average molecular weight $M_w$ and root mean square radius $R_g$ by light scattering, a Wyatt miniDawn Multi Angle Laser Light Scattering Instrument (MALLS) with a Wyatt Optilab 903 Interferometric Refractometer was used. The detectors used light at 690nm. from a diode laser in the miniDawn and from a filtered light source in the Optilab. This system was operated both with and without salt present in the mobile phase. Each sample was run in the system with no salt present, then the set was run with 0.02M Sodium trifluoroacetate salt (NaTFA) in the HFIP mobile phase. Solutions of PA-11, PMMA and PFA were made at roughly 5.0 mg/mL concentration. M-cresol was used as the solvent for PA-11 and PMMA solutions, and HFIP was used for PFA solutions.

Right Angle Laser Light Scattering

A second SEC system with HFIP mobile phase and 0.05M Potassium trifluoroacetate salt (KTFA) at a flow rate of 1.0ml/min with one Polymer Laboratories HFIPGel column at ambient temperature was used to characterize the PFA. Solutions of PFA in HFIP were made at roughly 2.5 mg/mL concentration. Using this salt-solvent SEC system measurements of $M_w$ and $R_g$ were taken with a Viscotek Triple Detector system: differential refractive index detection, viscosity, and
Single Angle 90° Laser Light Scattering (RALLS). The RALLS detector used light at 670nm.

Results and Discussion

*Poly (methylmethacrylate)*

The PMMA results shown in Figure 2 and Table II illustrate the typical unimodal peak obtained and the resultant accuracy of the HFIP system with a MALLS light scattering detector:

**Figure 2**

Typical PMMA Output, HFIP No Salt

Top: 90° light scattering

Bottom: Refractive Index
Table II
PMMA Analysis in HFIP No Salt System
Multi Angle Light Scattering

<table>
<thead>
<tr>
<th>Sample (MW)</th>
<th>Ret. Vol.</th>
<th>Mw</th>
<th>Mz</th>
<th>Mz/Mw</th>
<th>Rg</th>
</tr>
</thead>
<tbody>
<tr>
<td>2400</td>
<td>24.46</td>
<td>2080</td>
<td>3370</td>
<td>1.62</td>
<td>-</td>
</tr>
<tr>
<td>4910</td>
<td>23.47</td>
<td>4100</td>
<td>4350</td>
<td>1.06</td>
<td>-</td>
</tr>
<tr>
<td>6900</td>
<td>22.85</td>
<td>6150</td>
<td>6430</td>
<td>1.05</td>
<td>-</td>
</tr>
<tr>
<td>10000</td>
<td>22.38</td>
<td>9744</td>
<td>10070</td>
<td>1.03</td>
<td>-</td>
</tr>
<tr>
<td>28900</td>
<td>19.98</td>
<td>30660</td>
<td>31080</td>
<td>1.01</td>
<td>12.5</td>
</tr>
<tr>
<td>69000</td>
<td>17.78</td>
<td>70180</td>
<td>71300</td>
<td>1.02</td>
<td>13.1</td>
</tr>
<tr>
<td>212000</td>
<td>14.93</td>
<td>232400</td>
<td>246500</td>
<td>1.06</td>
<td>15.4</td>
</tr>
<tr>
<td>910500</td>
<td>12.98</td>
<td>913500</td>
<td>925600</td>
<td>1.01</td>
<td>49.3</td>
</tr>
</tbody>
</table>

As seen in Table II, the measured M_w values are quite close to those provided with the known standards. These results verify that MALLS is capable of absolute measurement of PMMA molecular weight over a range of roughly 10^3 to 10^6 Daltons. Use of a salt such as KTFA or NaTFA in the mobile phase is clearly not necessary for accurate determination of M_w in this case for PMMA.

**PA-11**

Figure 3 illustrates a representative unimodal peak typical in the MALLS and RI output for PA-11 in our system. As is the case with PMMA, we see good separation using the JordiGel DVB column. There is no evidence of distortion in the SEC chromatogram as has been reported in some studies of polyamides in HFIP due to a “polyelectrolyte” effect, and there is no reason therefore to expect error in the M_w calculations because of solution conformation. Even when there is chain extension, it is relevant to note the MALLS measurement of M_w is an absolute measurement.
regardless of the shape that the dissolved PA-11 molecule assumes in the mobile phase.

Veith and Cohen\cite{Veith1991} report a bimodal peak for PA-6 in HFIP without salt due to a "polyelectrolyte" effect. This is not seen for PA-11 in our HFIP system, as demonstrated in Figure 3. In fact, HFIP without salt has been previously demonstrated to be an effective and reliable solvent for PA-11.\cite{Veith1992, Veith1993} We suggest that the reason for the effect in PA-6 and not in PA-11 is due to the higher number of amide bonds per unit length along the chain backbone in PA-6. The relatively close proximity of the amide linkages in PA-6 gives rise to heightened repulsive forces and the resultant physical expansion of the chain from a relaxed coil to a more rigid form in solution.

**Figure 3**

Typical PA-11 Output, HFIP No Salt

Top: 90° light scattering  
Bottom: Refractive Index

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Table III  
PA-11 Analysis in HFIP, no salt  
Multi Angle Laser Light Scattering

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ret. Vol.</th>
<th>Mw</th>
<th>Mz</th>
<th>Mz/Mw</th>
<th>Rg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unplasticized PA-11 (15k)</td>
<td>21.728</td>
<td>15400</td>
<td>17460</td>
<td>1.13</td>
<td>6.3</td>
</tr>
<tr>
<td>Unplasticized PA-11 (30k)</td>
<td>21.501</td>
<td>29300</td>
<td>33640</td>
<td>1.15</td>
<td>18.0</td>
</tr>
<tr>
<td>Extruded PA-11 #1</td>
<td>20.287</td>
<td>41300</td>
<td>50780</td>
<td>1.33</td>
<td>16.7</td>
</tr>
<tr>
<td>Extruded PA-11 #2</td>
<td>19.408</td>
<td>57400</td>
<td>73300</td>
<td>1.28</td>
<td>25.4</td>
</tr>
<tr>
<td>Unplasticized PA-11 (72k)</td>
<td>17.056</td>
<td>72390</td>
<td>103200</td>
<td>1.43</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Figure 4  
PA-11, Mw(i) ~ 15k, unaged  
90° light scattering and representative slice Mw data  
Strip Chart - V628F3

Table III and Figure 4 show representative PA-11 molecular weight data, measured by the SEC-MALLS / HFIP system. As seen in Figure 4, MALLS detection calculates \( M_n \) slice by slice as the polymer elutes from chromatography and has a lower limit of approximately 7,500 Daltons for PA-11.

In addition to calculating molecular weights using light scattering measurements, a conventional plot of \( M_n \) vs. the retention volume peak using refractive index data from size exclusion chromatography can be constructed. The
accuracy of a calibration using this technique is severely limited by an assumption that the hydrodynamic radii for all of the polymers, both the standards and analytes, are consistent for all given values of $M_w$. Nevertheless, this technique can be useful in characterizing molecular weight distributions for polydisperse samples, especially those with appreciable amounts of low molecular weight polymer near or below the lower limit of detection by light scattering.

A plot of molecular weight vs. retention volume for the PMMA and PA-11 samples is provided in Figure 5. This plot shows the linear trend for PMMA and PA-11 retention volumes which are closely related, again indicating there is not a polyelectrolyte effect for the PA-11.

**Figure 5**
PMMA and PA-11 (commercial and unplasticized)
Retention Volumes in HFIP, no salt

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A universal calibration can also be used to estimate molecular weights based on a combination of viscosity measurements and retention volumes. However, in HFIP it has been previously and rather conclusively demonstrated that the universal calibration is not an improvement and does not work well for polymers such as polyamides and PMMA in HFIP.4

PFA

The poly(fluoro acrylate) or PFA, the focus of this study, has a unique structure compared to the PMMA and PA-11. In order to understand the behavior of the HFIP-solvated PFA molecules and the effect of the detection method the samples were studied in two detection systems and both with and without salt. Light scattering results from the multi-angle (MALLS) and the single-angle (RALLS) light scattering systems are reported in Tables IV and V. As stated earlier the RALLS system had KTFA salt in the HFIP mobile phase, while the MALLS system was run with no salt as well as with NaTFA salt.

As seen in the tables there is a noticeable difference between the two data sets, MALLS vs. RALLS. The calculated values for Mw and Rg from the SEC-MALLS system are consistently higher than the Viscosity-RALLS system. The values differ by a factor of up to nearly 2 for the PFA homopolymer set.
### Table IV
#### MALLS Results for PFA

<table>
<thead>
<tr>
<th>Sample</th>
<th>RV</th>
<th>Mw</th>
<th>Mz</th>
<th>Mz/Mw</th>
<th>Rg</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>12.27</td>
<td>29000</td>
<td>95900</td>
<td>3.31</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>11.144</td>
<td>114000</td>
<td>283000</td>
<td>2.48</td>
<td>8.5</td>
</tr>
<tr>
<td>4</td>
<td>10.489</td>
<td>199000</td>
<td>345200</td>
<td>1.73</td>
<td>16.9</td>
</tr>
<tr>
<td>5</td>
<td>10.139</td>
<td>666200</td>
<td>1158000</td>
<td>1.69</td>
<td>44.2</td>
</tr>
<tr>
<td>6</td>
<td>10.208</td>
<td>855000</td>
<td>1386000</td>
<td>1.62</td>
<td>48.4</td>
</tr>
<tr>
<td>8</td>
<td>10.054</td>
<td>1048000</td>
<td>1502000</td>
<td>1.43</td>
<td>54.7</td>
</tr>
<tr>
<td>9</td>
<td>10.139</td>
<td>894500</td>
<td>1646000</td>
<td>1.84</td>
<td>52.3</td>
</tr>
</tbody>
</table>

#### 0.02M NaTFA

<table>
<thead>
<tr>
<th>Sample</th>
<th>RV</th>
<th>Mw</th>
<th>Mz</th>
<th>Mz/Mw</th>
<th>Rg</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5.924</td>
<td>44650*</td>
<td>78570</td>
<td>1.76</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>2.771</td>
<td>122400</td>
<td>131100</td>
<td>1.07</td>
<td>27.1</td>
</tr>
<tr>
<td>4</td>
<td>2.692</td>
<td>227900</td>
<td>240100</td>
<td>1.05</td>
<td>24.8</td>
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<tr>
<td>5</td>
<td>2.618</td>
<td>846600</td>
<td>895500</td>
<td>1.08</td>
<td>48.6</td>
</tr>
<tr>
<td>6</td>
<td>2.596</td>
<td>1011000</td>
<td>1105000</td>
<td>1.09</td>
<td>51.8</td>
</tr>
<tr>
<td>8</td>
<td>2.58</td>
<td>1128000</td>
<td>1259000</td>
<td>1.12</td>
<td>57.1</td>
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<td>2.628</td>
<td>1103000</td>
<td>1164000</td>
<td>1.06</td>
<td>56.5</td>
</tr>
</tbody>
</table>

*high baseline noise

### Table V
#### RALLS Results for PFA

<table>
<thead>
<tr>
<th>Sample</th>
<th>RV</th>
<th>Mw</th>
<th>Mz</th>
<th>Mz/Mw</th>
<th>Rg</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>8.28</td>
<td>17850</td>
<td>37270</td>
<td>2.09</td>
<td>2.9</td>
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<td>2.38</td>
<td>5.7</td>
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<td>4</td>
<td>6.85</td>
<td>164600</td>
<td>417100</td>
<td>2.53</td>
<td>9.0</td>
</tr>
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<td>506300</td>
<td>891100</td>
<td>1.76</td>
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<tr>
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<td>641400</td>
<td>1101000</td>
<td>1.72</td>
<td>20.2</td>
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</tbody>
</table>

First, some notes on the data collection. In the first stage of this experiment, data was taken with the MALLS system without salt and on the RALLS system with salt. It was postulated that the difference in calculated $M_n$ values was due to a polyelectrolyte effect and an "aggregation" seen in the MALLS salt-free system but not in the RALLS salt system. It is known that localized charges on the polymer side...
groups can cause the polymer chains to become extended in solution. In a traditional SEC salt effect experiment, dissolved salt counteracts any polyelectrolyte effect, allowing the solvated polymer chains to relax into a near random coil state.

Without exhaustive salt and no salt data for both detector systems, the difference between the RALLS and MALLS data sets was postulated to be a result of this polyelectrolyte effect, chain extension due to interactions between the large fluorinated hydrophobic side groups. In addition it was hypothesized that these hydrophobic side groups are attracted to each other in the HFIP solution, resulting in chain pairs where the ends of each chain extend beyond each other due to partial chain overlap. In this working hypothesis the salt present in the RALLS system induces the chains to separate, resulting in the lower molecular weights calculated and corresponding values of $R_g$ of the single chain. This hypothesis was disproved after careful consideration of the two data sets as well as with the acquisition of additional data in a MALLS salt study.

The addition of salt into the HFIP mobile phase of the MALLS system caused an appreciable increase in baseline noise for light scattering. While this noise decreased the overall signal-to-noise ratio in the MALLS measurements, only in the case of sample 2 was this issue of serious concern. For the other samples, which have a much larger $M_w$ and thus scatter light with greater intensity, the large response of the polymer light scattering signal was much larger than the noise level in the baseline. Slightly higher values for $M_w$ seen in the MALLS-salt testing vs. the MALLS-no salt testing are the result of additional noise in the overall light scattering signal for the salt system.
**Discussion of Rg**

The MALLS system directly measures Rg using the angular dependence, $P_\theta$, of scattered light from the dissolved polymer. This technique is limited to molecules with $R_g$ of more than about 10nm for reasonable resolution, but the measurement requires no assumption about the shape or conformation of the polymer in solution nor its relation to the hydrodynamic volume. Only knowledge of the exact wavelength of light, $\lambda$, and the scattering intensity at each angle $\theta$ is used. The relationship between $P_\theta$, $\lambda$, and mean square radius is:\(^6\)

\[
\frac{1}{P_\theta} = 1 + \left( \frac{16\pi^2}{3\lambda^2} \right) \langle r_g^2 \rangle \sin^2 (\theta/2) \quad (1)
\]

Thus because MALLS measures light scattering at multiple angles simultaneously, this method is exact and preferable in cases where the conformation in solution is unknown.

For measurement of $R_g$ the RALLS system employs measurements of viscosity, which are related to the hydrodynamic volume of the polymer in solution. This viscosity data is then used to estimate $R_g$ via a series of assumptions, equations, and a combination with data from light scattering at one angle.

The light scattering equation relates polymer scattering through the excess Rayleigh Ratio - $R_0$, sample concentration - $c$, the second virial coefficient - $A_2$, $M_w$, and $P_0$ as:\(^6\)

\[
\frac{Kc}{R_0} = (M_w P_0)^{-1} + 2A_2 c \quad (2)
\]
Where $K$ is the traditional optical constant which includes the wavelength of light used $\lambda$, the refractive index of the solvent $\eta$, and the specific refractive index increment $\text{d}\eta/\text{d}c$.

The first assumption for this model is that the polymer is at infinite dilution in solution. This is a reasonable and practical assumption which allows the $2A_2c$ term to be dropped from the light scattering equation.

$$Kc / R_0 = (M_w P_0)^{-1} \quad (3)$$

Then a calculation of molecular weight can be made by assigning $P_0$ an initial iterative value of 1 and solving for $M_w$. Given that $P_0$ approaches unity for molecules with an $R_g$ of $\lambda/20$ or less, this is a reasonable assumption for small molecules. Particles of a size on the order of $\lambda/20$ or less scatter light in all directions equally. However, the angular dependency of light scattering for larger particles is significant. Thus the $P_0 = 1$ estimate is a significant source of uncertainty for this study, considering that many of the samples have an $R_g$ greater than $\lambda/20$.

The next assumption is that the polymer is in a random coil state in solution. This assumption is necessary to determine the angular dependency term $P_0$, as $P_0$ cannot be measured directly with only a right angle light scattering measurement. Assuming the random coil conformation in solution permits an estimate of the Mark-Houwink constant ‘$a$.’ But the conformation in solution is an unknown characteristic for the poly(fluoro acrylate) under study. The ‘$a$’ term is, in fact, unknown. As such
the assumption of a shape of the dissolved polymer molecule in solution is a source of uncertainty.

Nevertheless with this estimate of the Mark-Houwink constant, the Flory-Fox and Ptitsyn-Eizner formalisms\textsuperscript{6,7} can be used to estimate the value of Rg. This approach uses the experimentally measured viscosity - \( \eta \) and the first estimate of \( M_w \) from the modified light scattering equation (3):

\[
R_g = \frac{1}{6^{0.5}} \times ([\eta]M_w/F)^{1/3} \quad (4)
\]

where

\[
F = 2.86 \times 10^{21} \times (1 - 2.63\epsilon + 2.86\epsilon^2) \quad (5)
\]

and

\[
\epsilon = \frac{2(\alpha - 1)}{3} \quad (6)
\]

The use of equations (4), (5) and (6) introduces additional uncertainty in this approach. Equation (5) is susceptible to errors derived from these empirically determined universal constants which are not necessarily applicable to every polymer such as the PFA under study.

With an estimate of Rg and still assuming the random coil conformation, the angular dependence \( P_\theta \) can be back-calculated. The following relation is used:

\[
P(\theta)_\text{est} = \frac{2 \times (e^{-x} + x - 1)}{x^2} \quad (7)
\]

where

\[
x = 4 \times n_\text{o} / \lambda_\text{o} R_g \quad (8)
\]

and \( n_\text{o} \) is the refractive index of the solvent. Now this estimate of \( P_\theta \) is inserted into equation (3) for recalculation of \( M_w \) and the cycle is iterated until \( M_w \) and Rg no
longer change. Thus Rg and M_w in this approach are not directly measured but rather are based on a single angle light scattering measurement, an assumption of conformation and the applicability of the Flory-Fox and Ptitsyn-Eizner equations.

Discussion of Results

The PFA molecules in Samples 1, 2, and 3 are beyond the limit of detection for meaningful MALLS measurement of Rg. Nevertheless, both systems report clear trends in M_w and Rg which match changes in polymerization chemistry over the sample set. Samples 1 through 4 show increasing values for M_w and Rg, indicative of the decreasing amounts of chain transfer agent used in each polymerization. Much higher M_w and Rg values are reported for Samples 5, 6, 8 and 9, the samples polymerized without chain transfer agent.

Again looking at Tables IV and V, the differences in calculated values of M_w for each sample in the RALLS system with salt versus the MALLS system without salt were thought to reflect an extent of the aggregation due to a polyelectrolyte effect seen in HFIP mobile phase without salt. But a plot of ln Rg vs. ln M_w (Figure 6) suggests that roughly the same relationship between Rg and M_w holds for samples in both the pure HFIP and in HFIP with salt. This result suggests that the shape of the PFA is the same in HFIP regardless of salt content.
The slope of ln Rg vs ln Mw (Figure 6) for both the MALLS salt data and MALLS no salt data is 0.62. High for a random coil, but less than a that for a rigid rod. The triple detector viscosity determined Rg slope is 0.60, also high for random coil polymers. The slope for the MALLS data and the triple detector viscosity measured values for PFA solutions with and without salt present suggest that the polymer is in the same extended, rather stiff, coil state in both conditions. Moreover, the consistency in the results between MALLS with and without salt is evidence enough that the polyelectrolyte effect is not significant for this polymer in HFIP. (Ref Table IV) Yet the RALLS-calculated molecular weights are lower by a factor of two and Rg is 50% smaller than the value calculated by MALLS, strongly suggesting the method and assumptions used to calculate Mw using a single
right-angle detector coupled with viscosity and the Flory-Fox. Pititsyn-Eizner formalism are not valid for this PFA polymer system.
Conclusions

The consistent results for PMMA and PA-11 demonstrate that HFIP is an excellent solvent for use in Multi Angle Laser Light Scattering measurements of molecular weight for those polymers, with no evidence of a need for salt in solution. There is no effect of the presence of salt vs. no salt on chain stiffness for the PFA in HFIP. This behavior is evidenced by the linearity of the plot of ln Rg vs. ln Mw for both the no salt and salt systems and by the agreement between measured values of Mw by the MALLS detector in conditions with and without salt in the mobile phase. The PFA polymer is observed to be a relatively stiff random coil with an ‘a’ value of approximately 0.6. Differences in calculated values of Mw and Rg by Multi Angle Laser Light Scattering (MALLS) vs. Right Angle Laser Light Scattering (RALLS) are a function of the assumptions used in the RALLS method, and it appears the RALLS approach is not valid for this particular PFA polymer system.
References for Chapter 3


Chapter 4:

Characterizing and Modeling A Cage Effect During Hydrolysis of Polyamide-11

The following article describes an in-depth aging study of polyamide-11, PA-11, in aqueous aging environments. PA-11 has great importance in the petroleum industry as an inner layer / fluid barrier for pipes used in offshore oil drilling. This PA-11 barrier layer is exposed to an extremely rigorous chemical environment. The typical composition of fluid pumped up from under the ocean floor is 20% petroleum products, e.g. hydrocarbons, hot waxes, other organics, and 80% BS & W, or basic sediment and water. Either of these components, the organic portion or the aqueous portion, can contain harsh acids which are particularly damaging to PA-11 in the presence of water.

The PA-11 aging environments were carefully engineered to control for as many variables as possible, in order to isolate the driving forces behind the degradative hydrolysis reaction seen in PA-11 aging. This process included synthesizing our own PA-11 samples without the common plasticizers and additives which are included with commercial PA-11. The aqueous aging environments themselves were treated with extreme care and attention to detail, as described in the article, to ensure consistent chemical exposure.
Because of the complexity of not only the PA-11 material itself but also the use environment, characterizing PA-11 aging is a difficult task. Molecular weight measurement characterization techniques of polymers are generally performed in solution, but there are few known solvents for polyamides. In addition, only two of these are room temperature solvents for PA-11, namely 1,1,1,3,3,3-hexafluoropropanol (HFIP) and meta-cresol (m-cresol).

As shown in chapters 2 and 3, molecular weight characterization by Multi Angle Laser Light Scattering provides the most reliable and reproducible measure of molecular weight and size of any available macromolecular characterization technique today for all polymer systems. Application of this technique is necessary for total absolute PA-11 characterization. Thus an SEC-MALLS system was specifically designed and built for this purpose. The high viscosity of m-cresol at ambient temperatures makes m-cresol a poor choice for liquid chromatography, so HFIP was chosen as the mobile phase.

The finding of a quantifiable equilibrium molecular weight in PA-11 aging as reported in this chapter is a particularly important discovery. Previous extensive aging studies of PA-11 have concluded that the aging process resulted in continually decreasing molecular weights beyond the point of usefulness and even below the point of meaningful MW measurement by any technique. The discovery of an equilibrium molecular weight at a value near the mechanical failure point of approximately 25,000 Daltons is a vital discovery for several reasons:
• The existence of an equilibrium molecular weight strongly suggests that a competing reaction exists in the aging PA-11 material which counteracts the hydrolysis reaction.

• The competing reaction is a recombination reaction which is similar in chemistry to the polymerization reaction, and the reverse of the hydrolysis reaction.

• The data show that the rate of degradation slows as molecular weight approaches the equilibrium value. This suggests that a change in the chemistry of the PA-11 system is causing a change in the rates of the hydrolysis and recombination reactions.

• An aging experiment involving PA-11 with an initial molecular weight lower than the equilibrium value showed a net increase in molecular weight with exposure to the aging environment. This result proves the existence of a recombination reaction.

• Future aging experiments can target not only preventing the hydrolysis reaction but also enhancing the recombination reaction to create an environment which leads to a higher equilibrium PA-11 molecular weight. If these conditions could be matched or even approached in an actual use.
environment, a pipe with a quite extended or even an indefinite lifetime could be created. This has not been considered an attainable goal before now.

Bearing in mind that the health of the flexible piping, and specifically that of the PA-11 fluid barrier, represents the chief concern with respect to oil production from an offshore drilling endeavor and is often the rate-determining factor for recovery of found undersea oil reserves, the creation of an indefinitely healthy PA-11 material will have enormous ramifications in the offshore drilling industry.
Abstract. Multi Angle Laser Light Scattering (MALLS) is used to monitor changes in molecular weight during solid state aging of PA-11. A mathematical model is presented which successfully describes the degradation kinetics of PA-11 in pH7 water. The MALLS results demonstrate that there is a recombination reaction in the solid state, which may be described as a cage effect during hydrolysis-degradation of the amide bond. During aging, the competing recombination and hydrolysis reactions lead to the formation of an equilibrium molecular weight. The equilibrium molecular weight is surprisingly high at about 26,000 Daltons in pH7 water, a value close to the ductile-brittle transition. The activation energy of hydrolysis is 81 to 87kJ/mol, close to the values of previous acid degradation studies and a recent value of 96kJ/mol for hydrolysis of the peptide amide bond.
Introduction

Polyamides are among the most widely used synthetic polymers. Their stability both during polymerization and during fabrication has been widely studied. Most of the existing research on synthetic polyamide chains has focused on the degradation properties during synthesis and processing and particularly on short hydrocarbon polyamides such as PA-6. Here work has shown that in the presence of oxygen, oxidation can take place in the alkane chain at melt processing conditions. The presence of water is also important during polymerization as it can hydrolyze the amide bond limiting chain growth. In fact, water content controls the molecular weight during polymerization of PA-11, and not surprisingly the presence of moisture during melt processing results in hydrolysis and a reduction in the molecular weight. Thus the degradation properties of the amide linkage are an important subject in polyamides as well as polypeptides as this controls many biological processes.

Studies on the degradative stability of the polyamide bond during use of polyamide structures are more limited. The earliest references to degradation are in the presence of acids that show relatively rapid degradation at elevated temperatures and the interesting result that the rate of degradation actually folds over, becoming less, in extremely concentrated acid conditions. In recent years, the degradation of polyamides during use in less extreme acidic conditions has become an important subject.

Overall, much remains to be known about the hydrolytic processes governing the degradation of the polyamide bond in the solid state. Since past work has shown the processes to be quite complicated in acid media, it is appropriate to conduct a
systematic study of hydrolysis in a neutral pH7 environment to provide a fundamental basis for more complex environments and then to compare these results with past studies of hydrolysis of the amide bond in other polyamides as well as in polypeptides.

This report focuses on characterizing and modeling the degradation in molecular weight of the polyamide made from the condensation reaction of 11-aminoundecanoic acid, PA-11, in a neutral pH7 water environment over a range of temperatures from 90°C to 135°C. PA-11 has been selected as it is one of the most stable polyamides to degradation in the presence of water due to its long hydrocarbon chain. A complete understanding of its hydrolytic stability is critical to understanding its aging properties.

Today PA-11 is a particularly important polyamide as it is widely used as a polymer barrier for the transport of natural gas and crude oil. One of its most critical current applications is in flexible pipes connecting floating platforms to well heads on the ocean floor. As such, the stability or aging of the amide link in water and under relatively mild acidic conditions comparable to CO₂ and H₂S water conditions is of practical as well as a fundamental scientific interest.

The earliest study on the stability of the polyamide PA-11 is a conference paper.⁸ The paper described a wide range of properties which changed over time in mildly acidic, water, oil conditions such as stress and elongation at yield and failure, the heat of fusion, viscosity, sheer modulus, and gas permeability. In 1995, we reported after several years of aging experiments that the principal molecular mechanism causing a decline of all of these properties was hydrolytic cleavage at the amide bond of the PA chains.¹³,¹⁴ In addition, it was shown that the principal
measurement parameter that should be used to monitor aging of PA-11 should be molecular weight rather than mechanical properties which were then used. Simply stated, the mechanical measurements such as % elongation do not change a large amount until a critical time when the % elongation drops rapidly as the PA enters a ductile-brittle transition. On the other hand, the molecular weight as measured by viscosity, size exclusion chromatography (SEC) or light scattering decreases gradually and thereby provides an accurate means to monitor the rate and extent of hydrolytic aging throughout the entire lifetime of the PA-11’s use. Figure 1 shows the results from conventional SEC molecular weight measurements and percent elongation at break for six earlier studies in oil-water and water aging environments. pH 4 to 6 at 105°C for PA-11 mechanical testing samples, demonstrating the relationship between Mw and mechanical properties.
In 1997 and 1998, Verdu and co-workers published two papers using viscosity and conventional SEC on aging of commercial PA-11 samples in acid solutions.\textsuperscript{9,10} The first paper clearly showed that the diffusion of water into a solid PA specimen was quite rapid relative to the rate of hydrolysis. Thus, the two aging steps of water ingress and then degradation in samples less than 1 cm thick are controlled by the much slower rate of hydrolysis. These two papers also suggested that most of the hydrolysis occurs at the chain ends but that the chain cleavage process involves random chain scission. These two contradictory statements were explained by the proposal of chain recombination of the broken chains when the break is in the middle of a long chain, an affect that could be described as a cage affect where the broken
chain ends remain near each other. An attempt was made to model the complex exponential decay in molecular weight with modest success. During this time, the rate of hydrolysis in acid conditions was found in our laboratory to involve a complex exponential decay process such that the molecular rate of decay decreased more slowly than simple exponential decay as intermediate values of the molecular weight were achieved.\textsuperscript{14}

In order to better understand this degradation by hydrolysis process, a series of PA-11 samples of differing molecular weight ($M_w \approx 15,000$ to 78,000) have been synthesized. Each starting molecular weight has been aged at 4 temperatures 90°C, 105°C, 120°C and 135°C in a controlled pH 7 water environment in the absence of oxygen. The change in molecular weight was monitored with time over periods ranging up to one year using size exclusion chromatography with a multi angle laser light scattering detector.

**Experimental**

Samples of varying molecular weight PA-11 were synthesized from monomer, 11-Aminoundecanoic acid [CAS# 2432-99-7; 99%]. These samples contain no additives, plasticizers or detergents commonly used in commercial PA-11. in order to preclude the effects of these components on the hydrolysis process. These samples were made in an oven flushed with Argon gas, held at 190°C and under a reduced pressure of 380 torr. In order to control the molecular weight, reaction times were varied. For example, 12 hours for two high molecular weight samples ($M_w \approx 78,000$...
& 72,000 Daltons) and 1.5 and 0.75 hours for lower molecular weight samples ($M_w \approx 30,000$ & $15,000$ Daltons), where $M_w$ is the weight average molecular weight. These PA-11 samples of varying molecular weight were molded into plaques, and aging coupons $3\text{mm} \times 6\text{mm} \times 35\text{mm}$ were machined from the plaques. Surface material was cut off and from the aging coupons to avoid any possible effect of oxygen aging.

The pH 7 aging environments were prepared by bubbling deionized water with Argon for 30 minutes and sealing in heavy-wall glass #8648 Ace Pressure Tubes with the machined PA-11 coupons. The Oxygen concentration of the water was measured both by titration and with a Dissolved Oxygen detector. with Oxygen content of 0.5 mg/L and lower. Aging tubes were then placed in ovens or constant temperature baths at $90^\circ\text{C}$, $105^\circ\text{C}$, $120^\circ\text{C}$ and $135^\circ\text{C}$, and PA-11 coupons were removed at predetermined intervals.

Unaged and aged PA-11 coupons were dissolved in m-cresol for molecular weight analysis. Solutions were made at a concentration of ~5mg/mL using m-cresol which was distilled over glass beads. Solution heating to $70^\circ\text{C}$ with swirling over one hour promoted complete dissolution of the PA-11 into the solvent.

Molecular weight determinations were made in-line with Size Exclusion Chromatography. SEC. The mobile phase for the SEC system was 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), distilled over glass beads to ensure purity. Two JordiGel DVB Mixed Bed HPLC columns at 40°C were used for the separation. at a flow rate of 0.6mL/min maintained by a Waters 515 HPLC pump. Absolute molecular weight measurements of PA-11 were made by a Wyatt miniDawn Multi Angle Laser Light Scattering (MALLS) detector with a Wyatt Optilab 903 Differential
Refractometer. Both instruments made measurements at room temperature using monochromatic light at 690nm. from a diode laser in the miniDawn and from a filtered light source in the Optilab.

PA-11 solutions were injected in 100µL increments, and the Wyatt Astra software calculated absolute values of Mw from data taken by the MALLS system at a rate of eight measurements per second over the polymer peak elution. The SEC system shows excellent separation and an extremely high signal to noise ratio, as seen in Figure 2. The unimodal peak seen in this figure is an example of the unimodal peak shape consistently obtained by our SEC system for PA-11.

Figure 2
Typical PA-11 Output, HFIP mobile phase
Top: 90° light scattering
Bottom: Refractive Index
A previous analysis of PA-6 polyamides by Veith and Cohen indicated that a dissolved salt is necessary in HFIP mobile phase to obtain a unimodal peak.\textsuperscript{15} It is theorized that polymeric ions form along the polyamide chain which then repel each other, disrupting the solubilized chain conformation and leading to altered fractionation; excess salt ions in the mobile phase counteract the forces which lead to abnormal chain behavior. This "polyelectrolyte" effect is not observed for PA-11 in HFIP, however, neither by us or in a previous report.\textsuperscript{16} The HFIP mobile phase consistently yields unimodal polymer peaks as in Figure 2 without the addition of salt. Statistical workup of the resulting data slices over each unimodal polymer peak yielded Mn, Mw and Mz and a molecular weight distribution for the PA-11 samples. Figures 3a-b show the separation and values of Mw for two samples: unaged and aged low Mw(i) PA-11.

**Figure 3a**  
PA-11, Mw(i) ~ 15k, unaged  
90° light scattering and slice Mw data

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Figure 3b
PA-11, Mw(i) ~ 15k, aged 257 days in 90°C pH7 water
90° light scattering and slice Mw data
Mathematical Theory

Earlier work showed the degradation kinetics consisted of a combination of two first order kinetic processes, one rapid and one much slower. The work we report here suggests that the degradation process approaches an equilibrium between hydrolysis-chain scission and polymerization-recombination. The equilibrium reaction involving the Chain Scission Rate Constant $k_h$ and the Recombination Rate Constant $k_p$ is represented:

$$\text{CO}_2\text{H} + \text{NH}_2 \xrightleftharpoons[k_h]{k_p} \text{C} = \text{N} + \text{H}_2\text{O}$$

When hydrolysis-chain scission occurs at the amide linkage, solid-state polymerization or recombination can also happen as the acid end group combines with the nearby amine end group. Equilibrium is approached where the reaction rate of degradation-hydrolysis equals the reaction rate of recombination-polymerization. This hydrolysis equation is the result of the detailed elementary steps in hydrolysis of an amide bond.

One working assumption of this model is that the concentration of acid chain end groups equals the concentration of amine chain end groups, or $[R_2\text{NH}_2] = [R_1\text{CO}_2\text{H}]$. Since PA-11 is made from step condensation of monomer, there is a 1:1 ratio of acid end groups to amine end groups throughout the polymerization. It follows that if hydrolysis-chain scission of the amide linkage is the main degradation mechanism, each break in an amide linkage should result in one additional acid end
group and one additional amine end group. Thus the concentration of acid end groups should be equal to the amine end groups at all times.

The next assumption is that the amide concentration [-NHCO-] is large and may be assumed to be constant. This assumption is reasonable when we consider hydrolysis in the context of a solid state polymerization reaction. For example, assuming a starting PA-11 Mw of 60,000 Daltons and a Mw/Mn polydispersity equal to 2, the ideal theoretical value for PA-11, then Mn should be around 30,000 Daltons. The molar mass of the 11-aminoundecanoic acid monomer is roughly 200 Daltons, thus there are roughly 30,000/200 = 150 amide units per chain. If Mn decreases to 10,000 Daltons during degradation, it follows that hydrolysis-chain scission would occur at two amide sites per chain. The change in [-NHCO-] is just 2/150 = 1.33%, not a large amount.

Another assumption is that the water concentration is large and approximately constant. This means we assume that at a given temperature the water diffusion is much faster than the hydrolysis-recombination reaction, since a water molecule has much higher mobility than the end groups which are attached to the long polymer chains. Therefore the overall reaction rate is not determined by water diffusion rate unless the PA-11 sample is very thick. This fact is demonstrated in earlier PA-11 work of Verdu which shows that water diffusion occurs over a matter of a few days for samples with 1 cm or less in thickness for the temperatures of 90°C to 120°C used in this work. It is true that water concentration will vary a small amount with temperature and could depend on the crystallinity of the polyamide-11 samples. Any
significant changes in water concentration will lead to differences in the fit of the model.

Finally we assume that the influence of plasticizer is neglected. PA-11 for this study was made only from the monomer, without any plasticizer or additives.

The derivation is as follows:

\[
- \frac{d[-NH_2]}{dt} = - \frac{d[-CO_2H]}{dt} = k_r[-CO_2H][-NH_2] - k_0[-NHCO-][H_2O] \tag{1}
\]

When system reaches equilibrium.

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

Then

\[
k_r[-CO_2H][-NH_2] = k_0[-NHCO-][H_2O].
\]

And

\[
[-NHCO-][H_2O] = k_r c^2 / k_0 \tag{2}
\]

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

\[
[-NHCO-][H_2O] = k_r c^2 / k_0 \tag{3}
\]

Using the assumptions as shown in Appendix A we obtain

\[
M_{n_t} = M_{n_e} \left( \frac{1 + \frac{M_n^2 + M_z^2}{M_n^2 - M_z^2} e^{-\frac{M_n^2 - M_z^2}{M_n^2 - M_z^2}}}{\frac{M_n^2 - M_z^2}{M_n^2 + M_z^2} e^{\frac{M_n^2 - M_z^2}{M_n^2 - M_z^2}}} \right)^{0.5} \tag{4}
\]

and
\[ M_{w_i} = M_{w_e} \left( \frac{1 + \frac{M_w^2 - M_w^2}{M_w^2 - M_w^2} e^{J t}}{1 + \frac{M_w^2 - M_w^2}{M_w^2 - M_w^2} e^{J t}} \right)^{0.5} \] (5)

Where

\[ M_{w_e} = \frac{2\sqrt{M_o D}}{k_n \sqrt{k_r \left[ -NHCO - \right] \left[H_2O \right]}} \] (6)

and

\[ J = 2\sqrt{k_n k_r \left[ -NHCO - \right] \left[H_2O \right]} \] (7)

Assuming Arrhenius dependence.

\[ M_{w_e} = \frac{2\sqrt{M_o D}}{A_b \sqrt{A_r} e^{-E_a - E_r} \left[ -NHCO - \right] \left[H_2O \right]} \] (8)

and

\[ J = 2\sqrt{A_b \sqrt{A_r} e^{-E_a - E_r} \left[ -NHCO - \right] \left[H_2O \right]} \] (9)
Results & Discussion

Molecular Weight Data

Figure 4
Unplasticized Nylon md. 6/7/99 ~77k
105°C 100% DI Water pH7

Figure 5
Unplasticized Nylon md. 6/3/99 ~72k
105°C 100% DI Water pH7
Figure 6
Unplasticized Nylon md. 6/17/99 ~30k
105C 100% DI Water pH7

Figure 7
Unplasticized Nylon md. 6/28/99 ~15k
105C 100% DI Water pH7

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Figure 8

Unplasticized Nylon 90C
100% DI, Mw vs. Time

Figure 9

Unplasticized Nylon 105C
100% DI, Mw vs. Time

80

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Figure 10
Unplasticized Nylon 120°C
100% DI, Mw vs. Time

Figure 11
Unplasticized Nylon 135°C
100%DI Mw vs. Time
Figures 4-7 show the change in Mw versus time for four samples of varying initial molecular weight at 105°C in pH 7 DI water. The figures clearly illustrate that all four PA-11 samples tend toward a constant molecular weight after aging at 105°C. Figures 8-11 show PA-11 systems approaching equilibrium molecular weight at 90°C, 105°C, 120°C, and 135°C. The fact that all of these PA-11 systems approach approximately the same molecular weight value in these pH7 water environments strongly supports the hypothesis that two competing reactions exist, a degradative hydrolysis reaction mechanism competing with a recombination reaction, resulting in the apparent approach to an equilibrium molecular weight. For the high starting molecular weight PA-11. Figures 4 & 5, the rate of decrease in molecular weight is rapid in the earliest period of aging, then the decrease slows as the average molecular weight approaches equilibrium. This dominance by hydrolysis in the high molecular weight PA-11 arises from the fact that the concentration of amine and acid end groups, [-NH₂] and [-CO₂H], are extremely low relative to the large starting amide concentration, [-NHCO-]. Such conditions strongly favor hydrolysis over recombination because unreacted end groups are scarce in the high polymer and there is a relatively high concentration of reactive amide sites for hydrolysis. As the concentration of [-NH₂] and [-CO₂H] increase due to the resulting hydrolysis, recombination grows being continually more favored, leading to a net decrease in the rate of change in molecular weight. That is to say that hydrolysis still occurs but its effect on molecular weight is counteracted increasingly by the increasing rate of recombination. For these PA-11 samples the rates of hydrolysis and recombination
approach an equilibrium at a molecular weight of approximately 25,000 Daltons in pH 7 water at 105°C.

Figure 6 shows the far less dramatic change in molecular weight of the PA-11 sample with a starting molecular weight of 30,000 Daltons. In this sample [-NH₂] and [-CO₂H] are sufficient from the beginning of exposure to the pH7 water environment to allow for similar initial rates of hydrolysis and recombination. The data show a small gradual decline in molecular weight to the same 25,000 Daltons value as seen in the other PA-11 samples at 105°C.

Figure 7 also strongly supports the hydrolysis-recombination model as this PA-11 sample with a much smaller initial molecular weight of 15,000 Daltons starts with a higher concentration of amine and acid groups, giving rise to a dominance by recombination over hydrolysis upon exposure to the pH7 water aging environment. Figure 7 illustrates the rapid increase in molecular weight which slows with time as the sample approaches the equilibrium molecular weight value of 25,000 Daltons at 105°C. This slowdown in recombination arises from the decrease of [-NH₂] and [-CO₂H] in the sample as end groups are consumed by the reaction.

Analysis of the distribution of molecular weight in each sample leads to insight regarding the makeup of the aging PA-11 samples. We recall that the molecular weight values reported are weight average molecular weights, i.e. the statistical weighted average of each Mw data slice collected over the entire sample. A plot of the individual Mw slices plotted as weight fraction vs. molecular weight reveals the weight distribution of the sample. Figure 12a shows the molecular weight distributions for the four unaged PA-11 samples as measured using size exclusion
chromatography for separation and light scattering for measurement of polymer chain length for each eluting fraction. After 190 days of aging in 105°C pH 7 water not only do the weight average molecular weights of these samples approach the same value, but the distributions of molecular weights within each sample also converge. This effect illustrated in figures 12b and 13a-d and is strong evidence in support of the theory of a hydrolysis-recombination equilibrium.

Figure 12a
Unaged PA-11 Mw Distribution
Figure 12b
190 Days Aged PA-11 Distribution
105°C 100% DI Water pH7

Figure 13a
Unaged vs. Aged PA-11 Distribution
105°C 100% DI Water pH7, Mw(i) ~77k

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Figure 13b
Unaged vs. Aged PA-11 Distribution
105°C 100% DI Water pH7, Mw(i) ~72k

Figure 13c
Unaged vs. Aged PA-11 Distribution
105°C 100% DI Water pH7, Mw(i) ~30k

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These distribution plots (Fig. 13a-d and particularly 12b) reveal the same polymer distribution over the range of roughly 7,500 Daltons to more than 70,000 Daltons after aging in water, regardless of the widely varying starting molecular weight averages and distributions in the samples. Only with the presence of competing reactions which allow for both an increase and a decrease in molecular weight and which are controlled solely by reaction kinetics can such a reproducible end distribution be reached despite widely varying initial characteristics. Also noteworthy is the observation that the weight distributions for the aged PA-11 tend to become narrower, as compared with the distributions of the unaged material. This effect is most prominent in the high starting molecular weight material, where the highest Mw portions of the distribution are eliminated via hydrolysis. The end result
is a distribution closely centered on an equilibrium Mw value of approximately 25,000 Daltons. In the low starting molecular weight material the low Mw fractions are seen to recombine, but much higher Mw polymer does not form. Again the result is a distribution centered on about 25,000 Daltons. Admittedly, apparent narrowing in the weight distribution is due to the inability of the light scattering detector to detect polymer molecules below approximately 7,500 Daltons as was seen in Figures 3a-b.

Mathematical Fit: Kinetics

The molecular weight data from the pH7 water study at 90°C, 105°C, 120°C and 135°C were fit to the mathematical model using equation 5 to return the best values for Mw\textsubscript{equilibrium} and J for each polymer system. Representative results at 90°C-135°C are shown in Figures 14-28 and tabulated in Table I.
Figure 14
* Aging study of unplasticized PA-11
- polymer made 6/3/99 ~72k
- in 100% DI w/Ar 135C

Figure 15
*Aging Study of unplasticized PA-11
-polymer made 6/17/99 ~30k
-in 100% DI w/Ar, 135C

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Figure 16

* Aging Study of unplasticized PA-11
- polymer made 7/22/99 ~22k
- in 100% DI w/Ar, 135C

Figure 17

- Aging study of unplasticized Nylon
- polymer made on 06/07/99, MW~78k
- in 120C, 100%DIw/Ar

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Figure 18

- Aging study of unplasticized Nylon
- polymer made on 06/03/99, MW~72k
- in 120°C, 100% D/W/Ar

Days of Aging

Figure 19

- Aging study of unplasticized Nylon
- polymer made on 06/17/99, MW~30k
- in 120°C, 100% D/W/Ar

Days of Aging

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Figure 20

Aging study of unplasticized Nylon
- polymer made on 06/28/99, MW~15k
- in 120°C, 100%Dlw/Ar

Days of Aging

Figure 21

Aging study of unplasticized Nylon
- polymer made on 06/27/99, MW~78k
- in 105°C, 100%Dlw/Ar

Days of Aging
Figure 22

Aging study of unplasticized Nylon
- polymer made on 06/03/99, MW~72k
- in 105C, 100%DIw/Ar

Figure 23

Aging study of unplasticized Nylon
- polymer made on 06/17/99, MW~30k
- in 105C, 100%DIw/Ar

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Figure 24

Aging study of unplasticized Nylon
- polymer made on 06/28/99, MW~15k
- in 105°C, 100% DIw/Ar

Figure 25

Aging of unplasticized PA-11
- polymer made 6/3/99, Mw ~72k
- in 100% DI w/Ar, 90°C
Figure 26
Aging study of unplasticized PA-11
- polymer made 6/7/99 ~65k
- in 100% DI w/Ar, 90C

Figure 27
Aging Study of Unplasticized PA-11
- polymer made 6/17/99 ~30k
- in 100% DI w/Ar, 90C
Figure 28

Aging study of unplasticized PA-11
- polymer made 6/28/00 -15k
- in 100%DI w/Ar 90C

Table I
Mw(equilibrium) and J Results

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* These J values were fixed based on the average of the other values, as a good fit for both J and Mw could not be obtained by the fitting program.
Using equation 8, a plot of \( \ln (M_w^{(equilibrium)} )^2 \) vs. \( 1/T \) (Figure 29) shows that there is little temperature dependence on \( M_w^{(equilibrium)} \) within the scatter of the data. This can be compared to results observed during melt processing of PA-6. In melt processing, polymerization (recombination) is inhibited by the presence of the water, causing hydrolysis.\(^1\)\(^9\) It has been shown that in melt conditions lower temperatures lead to higher values of \( M_w^{(equilibrium)} \). The earlier work on melt processing of PA-6 in the temperature range of 235°C to 265°C reports a value for the activation energy difference of the equilibrium constant, \( K_p/K_h \), of \( E_p - E_h = -11.2 \text{kJ/mol} \).\(^9\) The temperature dependence in PA-6 melt processing, at 230°C to 300°C, can be compared with the PA-11 results in the solid state over the temperature range of 90°C to 135°C indicated in Figure 29. In Figure 29, the solid line represents the predicted relative temperature dependence observed during high temperature melt processing of the PA-6.\(^9\)

In the amorphous state, i.e. at temperatures of 90°C to 135°C, the much lower mobility of the polymer chains could inhibit the motion of reactive chain ends, increasing \( E_p \) relative to \( E_h \), inhibiting recombination and curtailing increases in molecular weight. Differences between the melt and solid state could lead to a lower temperature dependence of \( M_w \). This is suggested by the results in Table I and Figure 29 aside from one \( M_w^{(equilibrium)} \) value at 90°C. In addition approximately 20-30% of the polymer is in the crystalline state, representing regions of no chain mobility and an interfacial region of restricted mobility.
Using equation 9 in the equilibrium polymerization recombination model reveals the temperature dependence of the rate of change in $J$. A plot of $\ln J^2$ vs. $1/T(K)$, has a slope of $E_a/R$ equal to 19.650. Figure 30. Thus $E_a = 161$kJ/mol. This result is the sum of the activation energies for hydrolysis and polymerization, $E_h + E_p$. (equation 9) Assuming the variation in $M_w$ with temperature is approximately constant, $E_h$ and $E_p$ are approximately equal. then $E_h = E_p = 80.500$ kJ/mol. Given the uncertainty in the $M_w$ values of Figure 17, if we use the melt processing value of $E_p - E_h$ of $-6.5$ kJ/mol. then $E_h = 87$ kJmol. These values of $E_h$ can be compared with other $E_h$ values reported in the literature.
Jarrin et. al. report a hydrolysis energy of $E_a$ of $-110$ kJ/mol for PA-11 aging in pH6 to 7 water over a temperature range of 100°C to 150°C. This result is higher than the range of results, 70-110 kJ/mol, previously reported by Krisjuk.

Other studies on the rate of hydrolysis of the amide linkage in a variety of conditions also agree with the above results. Myagkov reports first-order rate of decay for homogeneous solution studies at 90°C to 118°C: caprolactam and PA-6 in sulphuric acid, $E_a = 84$ kJ/mol; caprolactam and PA-6 in NaOH, $E_a = 71$ kJ/mol; PA-6 in KOH, $E_a = 83$ kJ/mol.

It is particularly interesting to compare these synthetic polyamide hydrolysis results with the recently reported $E_a$ value for hydrolysis of the amide bond in several polypeptides in the absence of enzymes at pH5 to 7 conditions. Here Radzicka and
Wolfenden report $E_H$ to be 96 kJ, rather close to our 81 to 87 kJ value for the synthetic polyamide PA-11.\textsuperscript{7}

\textit{Acid Environments}

The role of pH is also to be explored. In the presence of excess acid, protonation of unreacted amine end groups significantly inhibits recombination of the amine with the carboxylic acids, resulting in a fraction of protonated amine chain ends which are much less reactive. Protonation of the amine ties up the lone pair of electrons on the Nitrogen atom, hindering nucleophilic attack by the amine on the acid group. Clearly this inhibits the rate of recombination and produces a lower value of $M_{w,e}$. Indeed lower molecular weights are observed in a preliminary study in water at pH3 and pH5 (HCl) as reported in Figure 20. After 60 days of exposure in pH3 and pH5 water at 120°C, the PA-11 has already fallen well below the equilibrium molecular weight of 25,000 for the 100% DI water pH7 study. The detailed behavior of PA-11 in an acidic water environment will be examined in future studies.
Figure 31

Unplasticized Nylon 6/3/99 72k 120C
Mw vs. Time

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Conclusions

Aging of solid high molecular weight PA-11 in pH7 water in the temperature range of 90°C to 135°C is due to hydrolysis of the amide bond. However aging studies of low molecular weight PA-11 show the molecular weight increases with time. Intermediate starting Mw's show little change with time.

These results suggest that degradation during aging actually involves two competing reactions, one hydrolysis and the other recombination. A simple model representing the hydrolysis and recombination rates fits the data well for starting molecular weights above and below the equilibrium value. For solid PA-11 in the 90°C to 135°C range there is little change or perhaps a small decrease in equilibrium molecular weight with increasing temperature, indicating $E_h$ is approximately equal to or slightly greater than $E_p$. The value of $E_h = 81$ to $87$kJ/mol for PA-11 in pH7 water is close to previously reported values for PA-6 in acidic conditions. And it is also interesting to observe that this activation energy for hydrolysis of a synthetic polyamide is quite close to the value of 96kJ/mol for polypeptide hydrolysis in the absence of enzymes at pH 5 to 7. Finally acidity protonates the reactive -NH2 group, inhibiting the nucleophilic recombination reaction and lowering $M_w(\text{equilibrium})$. 

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References for Chapter 4


18) Details of the model calculations are available as Appendix A from the authors.


Chapter 4: Appendix A
Mathematical Model

Nomenclature for the mathematical derivation is listed below:

1. $c_t$ – concentration of either amine end groups [-NH$_2$] or acid end groups [-CO$_2$H] at time $t$. unit: mol·L$^{-1}$

2. $c_i$ - the initial concentration of either end group. unit: mol·L$^{-1}$

3. $c_e$ – the concentration of either end group when system reaches equilibrium. unit: mol·L$^{-1}$

4. $a_t$ – the fraction of the remaining end group ([-NH$_2$] or [-CO$_2$H]) at time $t$. unitless

5. $a_i$ - the initial fraction of the remaining end groups, unitless

6. $a_e$ – the fraction of the remaining end groups 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 PA-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 groups in the system. unit: mol·L$^{-1}$

14. [$\text{H}_2\text{O}$] – the concentration of “effective” water inside the solid PA-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: $L^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

17. $A_h$ – Arrhenius frequency factor for hydrolysis reaction. unit: $J \cdot \text{mol}^{-1}$

18. $E_h$ – Activation energy for hydrolysis. unit: $L^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

The derivation is as follows:

\[
\frac{d[-NH_2]}{dt} = -\frac{d[-CO_2H]}{dt} = k_p[-CO_2H][-NH_2] - k_0[-NHCO-][H_2O] \tag{1}
\]

When system reaches equilibrium,

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

Then

\[
k_p[-CO_2H][-NH_2] = k_0[-NHCO-][H_2O].
\]

And

\[
[-NHCO-][H_2O] = k_p c_v^2 / k_n \tag{2}
\]

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

\[
[-NHCO-][H_2O] = k_p c_v^2 / k_n \tag{3}
\]

Equations (1) and (3) yield

\[
-\frac{dc}{dt} = k_p (c^2 - c_v^2) \tag{4}
\]

or

\[
-\frac{dc}{c^2 - c_v^2} = k_p dt \tag{5}
\]

Integrating $t$ from 0 to $t$, integrating $c$ from $c_0$ to $c$
\[ \int_0^t \frac{dc}{c^2 - c_i^2} = \int_0^t k_p dt \quad (6) \]

Hence,

\[ c_t = c_i \frac{c_c + c_t}{c_c - c_t} e^{2 \cdot \text{rate}} \]

\[ 1 + \frac{c_c + c_t}{c_c - c_t} e^{2 \cdot \text{rate}} \]

\[ (7) \]

Define the product of the amide bonds concentration and water concentration as \( B \), recalling this product is approximated as constant. \([-\text{NHCO-}] [\text{H}_2\text{O}] = B \), and from Equation (3) one obtains

\[ c_c = \sqrt{\frac{Bk_c}{k_p}} \quad (8) \]

Equation (7) can be written as:

\[ c_t = c_c \frac{c_c + c_t}{c_c - c_t} e^{2 \cdot \text{rate}} \]

\[ 1 + \frac{c_c + c_t}{c_c - c_t} e^{2 \cdot \text{rate}} \]

\[ (9) \]

define

\[ J = 2 \sqrt{\frac{Bk_c k}{h p}} = 2 \sqrt{\frac{k_c k}{h p}} [-\text{NHCO-}] [\text{H}_2\text{O}] \quad (10) \]

Equation (9) can be written as:

\[ c_t = c_c \frac{c_c + c_t}{c_c - c_t} e^{h} \]

\[ (11) \]

since for step condensation reaction

\[ c = \frac{am / M_n}{V'} = \frac{am / M_0}{1 - p} = \frac{a^2 \cdot m}{V'M_0} \quad (12) \]
Equation (11) turns into

$$a_i = a_e \left( \frac{a_c^2 + a_i^2 - \frac{a_i^2}{a_c^2 - a_i^2}}{1 + a_c^2 + a_i^2} \right)^{0.5} \left( \frac{a_c^2 - a_i^2}{a_c^2 + a_i^2} \right)$$

(13)

Using

$$M_n = \frac{M_e}{a}$$

where $$a = 1 - p$$

(14)

$$M_w = M_0 \frac{1 + p}{1 - p} = M_0 \left( \frac{2}{a} - 1 \right) \approx M_0 \frac{2}{a}$$

(15)

we obtain

$$M_{n_i} = M_{n_e} \left( \frac{1 + \frac{M_{n_i}^2 + M_{n_i}^2}{M_{n_i}^2 - M_{n_i}^2} e^{p_i}}{-1 + \frac{M_{n_i}^2 + M_{n_i}^2}{M_{n_i}^2 - M_{n_i}^2} e^{p_i}} \right)^{0.5}$$

(16)

$$M_{w_i} = M_{w_e} \left( \frac{1 + \frac{M_{w_i}^2 + M_{w_i}^2}{M_{w_i}^2 - M_{w_i}^2} e^{p_i}}{-1 + \frac{M_{w_i}^2 + M_{w_i}^2}{M_{w_i}^2 - M_{w_i}^2} e^{p_i}} \right)^{0.5}$$

(17)

An optimal parameter estimation program was developed and used to obtain the best-fit values of $$M_w$$ and $$J$$ for the proposed equation by using the experimental molecular weight data of the PA-11 aging study. A repetitive algorithm has been used where the objective function that has been minimized is given by

$$F'(x) = \sum_{i=1}^{N} \frac{|M_w, exp(i) - M_w, theor(i)|}{M_w, theor(i)}$$

(19)
Equations (8), (12), (15) yield

\[
Ce = \sqrt{\frac{[-\text{NHCO-}][\text{H}_2\text{O}] k_h}{k_p}} = \frac{a_2^m}{M_0 V} = \frac{\left(\frac{2M_0}{M_w^c}\right)^{\frac{1}{2}} D}{M_0}
\]  

(20)

Where \( D = \frac{m}{V} \).

Rearranging Equation (20), we obtain

\[
M_w^c = \frac{2\sqrt{M_0 D}}{\sqrt[4]{k_h [-\text{NHCO-}][\text{H}_2\text{O}]}}
\]  

(21)

while Equation (10) gives us

\[
J = 2\sqrt{k_h k_p [-\text{NHCO-}][\text{H}_2\text{O}]}
\]  

(22)

Equation (21) suggests that the molecular weight of the PA-11 will reach equilibrium at a given temperature, regardless of the initial molecular weight. Since the density of PA-11 is relatively constant in the range of molecular weights examined, and we assume that [-NHCO-] and [H\(_2\)O] are constant, then \( M_w^c \) should only depend on the ratio of \( k_h/k_p \).

Equation (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 \( k_h k_p \).

From the Arrhenius equation:

\[
k_h = A_h e^{-\frac{E_a}{RT}}
\]  

(23)
\[ k_p = A_p e^{-E_p/RT} \]  

Equation (21) can be written as

\[ M_w = \sqrt[2]{\frac{2M_0D}{\int A_p e^{\frac{\mu_n}{RT}} [-\text{NHCO}][\text{H}_2\text{O}]}} \]  

Equation (22) can be written as

\[ J = 2\sqrt{A_nA_pe^{-\frac{\mu_n}{RT}} [-\text{NHCO}][\text{H}_2\text{O}]} \]  

Using the experimental data at each temperature (135°C, 120°C, 105°C, and 90°C), the temperature dependence of \( M_w \) (\( M_w(T) \) vs. T) and \( J(J(T) \) vs. T) can be determined. Hence, for a given temperature, we can determine the values of \( M_w \) and \( J \) from these plots and then by using the equation (17), it is possible to predict the molecular weight of PA-11 after aging at any given time, and at any given temperature within the temperature range studied.
Introduction

The pH7 water study has demonstrated that the molecular weight of PA-11 will increase or decrease toward a temperature dependent equilibrium molecular weight value at 90°C, 105°C and 120°C. The changes in PA-11 molecular weight result from two competing reactions, the hydrolysis-degradation reaction and a recombination-polymerization reaction. A preliminary follow-up study involving pressure and acid content has been conducted to verify the assumptions made in the pH7 study and to assess the validity of the acid-catalyzed hydrolysis mechanism and the recombination mechanism.

In the pH7 water study the rate of the hydrolysis-degradation reaction was not targeted for control. Both the reactive amide units, [-NHCO-], and the effective water concentration, [H$_2$O], inside the PA-11 were assumed to be large and approximately constant. Given the equilibrium reaction (1)

\[
\begin{align*}
\text{CO}_2\text{H} + \text{NH}_2 & \rightleftharpoons \text{C-N} + \text{H}_2\text{O} \\
& k_p \quad k_h
\end{align*}
\]

changes in the concentration of acid end groups, [-CO$_2$H], and amine end groups, [-NH$_2$], caused the equilibrium PA-11 molecular weight to be reached. For example in the case of high starting molecular weight PA-11, [CO$_2$H] and [-NH$_2$] are below equilibrium. In this case hydrolysis predominates, resulting in an approach to equilibrium molecular weight and higher concentration of end groups. Conversely
with low starting molecular weight PA-11. \([\text{CO}_2\text{H}]\) and \([-\text{NH}_2]\) are higher than the equilibrium value, favoring recombination and leading to a decrease in end group concentration and an increase in molecular weight toward equilibrium.

**Pressure Study**

In a follow-up pressure study we tested the assumption that \([\text{H}_2\text{O}]\) is large and constant, an approach which targeted the hydrolysis-degradation side of the equilibrium reaction (1). Under controlled pressure conditions the role of water ingress was analyzed by attempting to increase or decrease the rate of hydrolysis based on \([\text{H}_2\text{O}]\).

**Acid Study, Water Present**

A study involving organic acid in the aging environment was conducted to examine the change in equilibrium molecular weight as a function of acid content. This study targeted both the hydrolysis and recombination reactions. With water present the acid-catalyzed hydrolysis reaction is relatively more favored in lower pH environments vs. in the neutral pH7 water environment from the earlier PA-11 study. Additionally the reactive amine end groups can be protonated by excess acid present in the aging environment. Protonation of amine end groups then leads to a decrease in the effective concentration of reactive amine end groups, thus inhibiting recombination.
Acid Study, No Water Present

A study involving organic acid but with no water present tests the theory that hydrolysis is the mechanism for degradation in PA-11. In the absence of water hydrolysis cannot occur. thus if hydrolysis is the only mechanism for PA-11 degradation at the temperature range of our studies then the molecular weight will not decrease in the absence of water at a typical aging temperature.

Experimental

The aging studies were conducted by Norsk Hydro, and both unaged and aged samples were sent to William & Mary for SEC-LLS analysis. The PA-11 used for these studies was commercial PA-11. Rilsan P40TL.

For the pressure experiment the PA-11 coupons were exposed to 125°C 100% water environments purged with Nitrogen gas. Two pressure environments were used, 4 bar and 400 bar.

The acid studies were conducted at 115°C with samples aging in a liquid decane phase. A water phase was also present, and the environments were purged with Nitrogen gas. Acid concentrations of 10wt%, 1wt% and 0.1wt% naphthenic acid were used. The acid study without water was also conducted at 115°C. with 1wt% naphthenic acid but no water phase present.

Unaged and aged samples were prepared for molecular weight analysis using the same procedure as for the pH7 water study and analyzed using the same SEC-LLS system.
Results and Discussion

Pressure Study

Figure 1 shows the SEC-LLS results for the PA-11 pressure study. The molecular weight values for both the 4 bar and 400 bar water aging environments at 115°C are quite similar, suggesting that pressure does not appear to have an appreciable effect on the rate of change in Mw in a water aging environment.

Figure 1
Norsk Hydro Pressure Study
115°C 100% Water
Acid Study, Water Present

Figure 2 plots the results for the wet and dry acid PA-11 aging environments. As seen in the plot, higher concentrations of acid in the wet decane aging environments lead to faster degradation kinetics and lower equilibrium values for Mw. This lowering in Mw is the result of two additive effects: an increase in the acid-catalyzed hydrolysis reaction (Figure 3) and a modified equilibrium condition which is subject to protonation of reactive –NH₂ end groups (Figure 4). In the 10wt% acid environment, hydrolysis appears to dominate so strongly that a clear equilibrium Mw is not reached in the time scale of this experiment. It is possible that an equilibrium Mw will not be reached for PA-11 aging in a water environment with excess acid present.
Figure 2
Norsk Hydro Acid Study
115°C Decane Phase

- 10% acid  
- 1% acid  
- 0.1% acid  
- 1% acid, dry
Figure 3
Hydrolysis Mechanism

Step 1

Step 2

Step 3

Step 4

Step 5

Step 6

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Acid Study, No Water Present

In the dry decane acid aging environment a marked increase in Mw is observed. In this environment recombination dominates due to the absence of water necessary for hydrolysis to occur. It is interesting to note that the equilibrium molecular weight reached in this system is the same as that reached when 11-aminoundecanoic acid, the monomer for PA-11, is polymerized in inert, dry conditions at high temperature (>190°C) for several hours. The value of ~77,000 Daltons is the highest molecular weight obtained in the synthesis of unplasticized PA-11 for the pH7 water study. At this high molecular weight [CO₂H] and [-NH₂] are so low that recombination is greatly inhibited by spatial separation within the semi-crystalline PA-11 matrix. Because portions of the polymer chains are anchored in crystalline regions, at low concentrations the sparse reactive end groups cannot move close enough together to react.
Conclusions

These preliminary studies on the effect of acid and pressure on the aging of PA-11 support the working model of two competing reactions, hydrolysis-degradation and recombination-polymerization, in PA-11 during aging at elevated temperature, ca. 100°C. Pressure has little or no effect on the rate of change in Mw, and the assumption that [H₂O] is large and relatively constant during PA-11 aging is valid in an environment with water present. Higher concentrations of acid lead to more rapid hydrolysis and a lower equilibrium value of Mw when water is present in the aging environment. Finally recombination can dominate in dry conditions even with trace acid present, resulting in a significant increase in Mw.

Additional studies involving the unplasticized PA-11 in acid aging environments are underway. Data collected from unplasticized PA-11 aging systems will be compared with the results presented here, from commercial plasticized PA-11, to further characterize the hydrolysis-recombination equilibrium, to further understand PA-11 aging in acid environments, and to begin to understand the role of plasticizers in PA-11 aging.

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Chapter 4: Appendix C
SEC-MALLS Mw Data

### Unplasticized PA-11 Mw(i)~78k, pH7 water, 90C

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Chapter 5:

Moisture-Curing Kinetics of Isocyanate Prepolymer Adhesives

Abstract.

The reaction between isocyanate terminated prepolymers and atmospheric moisture produces urea linkages, which results in a hydrogen-bonded network of linear high molecular weight polymers with adhesive properties. This study describes the synthesis of isocyanate-terminated prepolymers and investigates the use of in-situ infrared spectroscopy as a technique for monitoring the chemistry of the polymerization reaction kinetics. In-situ FTIR was successfully used as a means to monitor the residual isocyanate levels and the extent of the polymerization reaction. Frequency Dependent Dielectric Measurement Sensing (FDEMS) using a thin, planar sensor has been used to monitor the reaction kinetics by monitoring changes in the mobility at the molecular level of ions in the reacting medium. A direct correlation of the prepolymer cure was found between the normalized FTIR isocyanate absorbance spectrum and the FDEMS permittivity at 500 Hz for the duration of the cure cycle. The results of this investigation show how FDEMS is an effective online method to monitor the extent of moisture cure in the bulk as well as in a coating or adhesive bondline, and thereby the resulting buildup in performance properties of the reactive liquid polyurethane adhesive.
Introduction

Isocyanate terminated prepolymers react with atmospheric moisture to form hydrogen bond cross-linked polymeric adhesives.\textsuperscript{1-3} The resulting adhesives are generally used to form moisture, heat, and solvent resistant bonds with porous materials that contain inherent moisture. This study involves the preliminary investigation of moisture curing isocyanate prepolymers and the cure kinetics associated with these adhesives. Previous FTIR spectroscopy cure studies have focused on the consumption of isocyanate levels near the prepolymer and air interface during covalent cross-linking reactions.\textsuperscript{4-6} The emphasis of this paper is concerned with the formation of the hydrogen-bonded network within the bulk due to urea linkage formation. FTIR and dielectric measurements have been used in concert to monitor polymer chain extension during the moisture curing process.\textsuperscript{7-9}

The cure of urethane prepolymers results from the reaction between isocyanate end groups with hydroxyl terminated molecules such as water to form urea linkages. The reaction proceeds through a carbamic acid intermediate and dissociates to form carbon dioxide and an amine, which is shown in Scheme 1.\textsuperscript{1,2} The objective of this study is to determine an effective test method that can be used to monitor cure kinetics of the diffusion of moisture into the prepolymer and the formation of the urea linkages within the polyurethane during cure. Another objective is determining whether moisture diffusion is the rate-determining step during the cure process and what chemical and environmental factors influence the relative moisture uptake and corresponding reaction rates.
The dielectric impedance of a material can be measured in order to monitor changes at the molecular level, which correlate with changes in macroscopic mechanical properties\textsuperscript{10-14}. In dielectric measurements the two-parameter complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ is calculated from frequency dependent measurements of the capacitance $C$ and the conductance $G$ according to the following equations:

$$\varepsilon'(\omega) = \left[ \frac{C(\omega)_{\text{material}}}{C_0} \right]$$

and

$$\varepsilon''(\omega) = \left[ \frac{G(\omega)_{\text{material}}}{\omega C_0} \right]$$

where $\omega = 2\pi f$, $f$ is the measurement frequency, and $C_0$ is the air replacement capacitance of the embedded micro sensor.

The conductivity, $\sigma$, of ions in the curing system is a function of the number of particles, $N_i$, times the particle mobility in the medium, $\mu_i$, or $\sigma = \sum N_i \mu_i$. It is calculated from FDEMS measurements when the product of $\omega \varepsilon''(\omega)$ is constant using the relation

$$\sigma = \varepsilon_0 \omega \varepsilon''(\omega)$$

where $\varepsilon_0$ is the permittivity of free space, 8.85 pF/m. The product of measurement frequency ($\omega$) multiplied by the imaginary component of the dielectric permittivity $\varepsilon''(\omega)$ can thus visually and quantitatively be used to monitor changes in ionic...
mobility when ε" is dominated by the mobility of ions as verified by overlapping values of ωε"(ω).

**Experimental**

*Materials*

Dow Chemical Company generously supplied poly(propylene glycol) having a hydroxyl number of 56.4 and an average functionality of 1.8 in addition to 4-4′-methylenebisphenyl isocyanate (MDI). The polyol was dried at 120°C in the reaction flask under vacuum and constant agitation for two hours prior to synthesis. The MDI was melted at 50°C prior to being added to the reaction flask. The catalyst, dibutyltin dilaurate (Dabco T-12) was supplied by Air Products and was used as received.

*Prepolymer Synthesis*

Four prepolymers were synthesized for this study. Samples with four and ten weight-percent residual isocyanate level without catalyst and samples of both four and ten weight-percent residual isocyanate level containing 0.004 weight percent catalyst were synthesized. For example, a 2.2 isocyanate to hydroxyl molar ratio was utilized to prepare a 4 weight percent isocyanate level. A three-necked 500mL flask was used for synthesizing the urethane prepolymers. A glass mechanical stirring rod was placed in the center port while a vacuum line was placed in the second port. A thermocouple and a nitrogen line were both sealed in the third neck within a septum. The temperature of the reaction was controlled using a heating mantle. Prior to the addition of the polyol to the reaction flask, all of the glassware was dried in a vacuum
oven at 120°C. The polyol (117.51 g, 0.1181 mol) was charged to the reaction vessel and was dried in the reaction flask at 120°C under vacuum for 1 hour. The reaction flask containing the dried polyol was cooled to 75°C under constant agitation and a nitrogen purge. The melted MDI (32.49 g, 0.2599 mol) was then charged into the reaction flask using a syringe. The temperature in the reaction vessel increased to 85°C during the first few minutes, but was maintained at 80°C for the remaining duration of the two-hour reaction period. At this point, 0.004-weight percent dibutyltin dilaurate catalyst (5.8 mL) was added to samples prepared with catalyst. At the completion of the reaction, the prepolymer was then titrated to insure that the correct isocyanate level was achieved and was stored in a dessicator inside a container that was purged with argon.

Characterization

ASTM D 2572-91 titration procedure for urethane prepolymer was used in conjunction with in-situ mid-infrared spectroscopy to accurately monitor the residual isocyanate functionality levels throughout the polymerization. Mid-infrared spectra were recorded at a rate of two scans per minute during the prepolymer polymerization until the reaction endpoint had been reached. The infrared spectra were collected using an ASI ReactIR 1000 in-situ fourier transform infrared spectrometer equipped with ASI data acquisition software. The reaction flask setup used for the IR data collection remained the same except for the addition of a fourth neck, which was used as the IR probe port.
Specimens for FDEMS cure studies were made by applying a 0.025 mm film of prepolymer onto a DekDyne interdigitated planar sensor with dimensions of $1\frac{1}{2}$ inches and 5mm thick in an argon purged atmosphere bag using a BYK-Gardner film casting knife blade. The FDEMS measurements were collected using a Hewlett Packard impedance bridge controlled with data collecting software. Continuous measurements of capacitance, conductance, and temperature were taken at ten frequencies from 5 Hz to $5 \times 10^5$ Hz throughout the entire cure process. The real and imaginary components of the complex permittivity were then calculated and recorded for each frequency. Five sample conditions were prepared using prepolymer with four and ten weight-percent residual isocyanate levels as well as a methanol-deactivated sample at ambient temperature and 40% relative humidity. The environmental conditions for each sensor are reported in Table 1. The 40% relative humidity chambers used to control the humidity environment were made by mixing $K_2SO_3$ and water in the bottom of a dessicator.

An FTIR study of the curing 4% NCO prepolymer without catalyst was conducted using a MIDAC M-series FTIR to record spectra at selected time intervals during cure. Prepolymer was applied to NaCl plates using a BYK-Gardner film casting knife blade to produce a 0.025 mm thick film. The coated salt plate was then placed in a 40% relative humidity chamber until a spectrum was collected. For each FTIR scan, the plate was placed on a fixture in a vertical position within the instrument's nitrogen purged atmosphere. The sample was placed back into the humidity chamber following the scan until the next measurement was collected. The
coated plate remained in the vertical position within the instrument for approximately 60 seconds for each recorded spectrum.

**Results and Discussion**

Figure 1 shows a three-dimensional waterfall plot of the urethane carbonyl absorbance (1724 cm\(^{-1}\)) versus time during the urethane prepolymer polymerization, which did not contain catalyst. The growth in the absorbance as a function of time can be used to monitor the conversion of isocyanate functional groups to urethane groups during the reaction. The plot shows that the bulk of the carbonyl absorbance growth was finished after the normal two-hour reaction period, but further carbonyl formation was evident. This is presumably due to urea-forming side reactions resulting from the reaction of residual isocyanate groups and any moisture that may have diffused into the reaction flask around the IR probe joint. It is also useful to monitor the simultaneous decrease in the isocyanate absorbance peak at 2272 cm\(^{-1}\) and the increase in amide II absorbance at 1525 cm\(^{-1}\).

Figure 2 shows the waterfall plot of the isocyanate consumption absorbance at 2272 cm\(^{-1}\). This plot shows that the isocyanate levels continue to decrease well after the normal reaction time. Profiles of the isocyanate and urethane carbonyl peaks shown in Figure 3 show that a urea forming side reaction was taking place during the data collection due to water ingress. This was attributed to the reaction flask that was used in order to allow the IR probe to be placed into the flask during polymerization.

Titration measurements recorded during and immediately preceding the polymerization reaction verified the formation of urea and the steady consumption of
isocyanate end groups. Although our primary goal was to produce urethane prepolymer without the presence of urea linkages, it was found that the *in-situ* FTIR provided a valuable method for identifying isocyanate side reactions early during prepolymer polymerization.

The FDEMS studies of the isocyanate prepolymer were significantly easier to conduct than the FTIR experiments and thus a series of environments were examined. Figures 4a-d show the results of FDEMS in-situ sensor measurements of the change in log ε"(ω) for four reacting systems at ambient temperature and 40% humidity: 4% NCO with and without catalyst and 10% NCO with and without catalyst. All of the systems show a relatively low conductivity as observed by the small overall values for log [ωε"(ω)].

A related FDEMS study of pure cyanate cure in our laboratory with a similar value of log [ωε"(ω)] has demonstrated that the mobility of residual impurity ions is being monitored in the dielectric measurement of the cyanate and that the number of these residual ions is constant over cure. This effect was verified by doping the cyanate reactant with a known concentration of ions. The cure chemistry of the isocyanate prepolymer adhesive suggests neither the creation nor consumption of ions (Scheme 1). Furthermore the relatively low level of ωε"(ω) compared to epoxy and polyamide systems of higher viscosity and its comparable value to the cyanate cure suggests that proton transfer is not a major mechanism for conduction. Conductivity is a function of the number of ions and their mobility, $\sigma = \sum N_i \mu_i$. When the number of ions $N_i$ can be assumed to be constant, then as in this case changes in conductivity are dominated by the changes of the ionic mobility during cure of the isocyanate system.
These changes in conductivity are monitoring the decrease in mobility of the curing system and the corresponding increase in viscosity with the buildup of the urea network.

FDEMS measurements of $\varepsilon''(\omega)$ can be used to monitor the reactive process. For example, FDEMS plots of $\log \omega \varepsilon''(\omega)$ for the 4% NCO catalyzed and uncatalyzed systems suggest a time for completion of cure of about 600 minutes because at this point $\delta \varepsilon''(\omega)/\delta t$ reaches 0. No change in the conductivity with time suggests that the mobility of the ions in the system is constant and a full cure state for this temperature has been achieved. A postcure study at 120°C showed little or no change in $\omega \varepsilon''$ after the system reached postcure temperature, verifying that the system had indeed reached full cure. Furthermore the initial slope of $\delta \omega \varepsilon''(\omega)/\delta t$ for the catalyzed system is higher than that of the uncatalyzed system. This rate of change in $\omega \varepsilon''$ is monitoring the faster initial reaction rate for the catalyzed system.

The 10% NCO catalyzed and uncatalyzed systems show a greater difference in the time for reaction completion. The catalyzed system reaches $\delta \varepsilon''(\omega)/\delta t = 0$ at 500 minutes, while $\delta \varepsilon''(\omega)/\delta t$ approaches zero for the uncatalyzed system at about 800 minutes. As in the 4% NCO study, the initial rate of cure is faster for the catalyzed system as monitored by $\delta \varepsilon''(\omega)/\delta t$ during the initial minutes.

Thus this study qualitatively shows that the uncatalyzed prepolymer systems containing 4% residual isocyanate levels reaches full cure at a greater rate than the systems containing 10% residual isocyanate levels, and the initial cure rate for both systems are increased with the addition of dibutyltin dilaurate catalyst. The data leads
us to believe that the addition of the dibutyltin dilaurate catalyst increased the water uptake rate of the prepolymer during the initial 40% relative humidity exposure. Also, the decreased cure rate of the uncatalyzed prepolymer containing 10% residual isocyanate can be attributed to the increased reaction rate on the surface of the prepolymer, which further decreases the diffusion rate of moisture into the prepolymer.

An additional dielectric study was carried out on a methanol-deactivated prepolymer. At the conclusion of polymerization, an excess of methanol was stirred into the prepolymer in order to react with the moisture reactive isocyanate end groups. An FDEMS experiment was run with this sample, and plots of the real and imaginary components of permittivity as a function of time are shown in Figures 5a-b. A change in ionic mobility is observed over time for the deactivated system. The net decrease in both the permittivity and the imaginary component's conductivity reflects a decrease in ionic mobility as the system equilibrates with the 40% humidity environment. If significant amounts of proton conduction were present, an initial increase in $\omega\varepsilon''(\omega)$ and $\varepsilon'$ would occur. This is not observed. The diffusion equilibrium process results in a decrease in $\varepsilon'$ and $\omega\varepsilon''(\omega)$. The time for this process to reach completion is approximately 500 minutes. This time is close to the cure time and suggests that gas diffusion in the prepolymer is a rate-controlling step affecting adhesive cure, the buildup in viscosity, adhesive strength and the corresponding decrease in ionic mobility. Thus, using FDEMS measurements of deactivated systems may lead to the determination of initial moisture diffusion rates in moisture-curing prepolymer systems.
FTIR was used as an additional method to monitor the rate of cure of a film by following the urea forming reaction by measuring the decrease in the isocyanate absorbance peak at 2272 cm\(^{-1}\) as a function of time. Many attempts were made to devise a method to accurately use FTIR spectroscopy for following the cure reaction in the bulk. However, the collected data was influenced by viscous flow on the surface of the NaCl plate because the FTIR plate had to be placed vertically in the instrument for data collection. ATR-FTIR could have been used to monitor the reaction at the surface of the prepolymer, but we were interested in a comparison of bulk properties with the FDEMS data. Figure 6 shows the spectrum from the non-catalyzed 4% residual isocyanate prepolymer cure as a function of time in a 40% relative humidity chamber. The plot reveals that the isocyanate absorption decreased at a decreasing rate throughout the cure period as a result of urea formation and the developing hydrogen bond adhesive network. This data coupled with the FDEMS data on the deactivated polymer qualitatively support the concept that during prepolymer cure, both the mobility of diffusing moisture in the prepolymer and the cure rate decrease. Finally the direct correlation between the imaginary component of permittivity computed at 500 Hz. and the disappearance of the isocyanate using FTIR was examined. Figure 7 depicts this correlation. The extent of cure was calculated with the FTIR data by dividing the difference in the NCO absorbance and a constant baseline absorbance at a given time by the difference in the NCO absorbance and the constant baseline absorbance point prior to the moisture cure reaction. The FDEMS extent of cure was calculated by subtracting the ratio of the difference of the imaginary permittivity component at a given time and the initial imaginary
permittivity and the difference of the final imaginary permittivity and the initial imaginary permittivity. The FTIR and FDEMS data collected from the cure of the uncatalyzed 4% residual isocyanate prepolymer were both recorded under the same environmental condition, however the FDEMS technique has the advantage of online in-situ monitoring throughout the curing process in both a laboratory environment and during cure of a coating\textsuperscript{12,13} or in an adhesive bond line\textsuperscript{14} in any environment. Future investigations will involve a more complete understanding of the role of $\varepsilon''(\omega)$ versus kinetic rate for moisture curing urethane prepolymer.

**Conclusions**

Urethane prepolymer reactions can be successfully monitored using *in-situ* FTIR and titration during the synthesis of prepolymer with various residual isocyanate levels. Titration data confirmed that the absorbance peaks from the formation of the urethane carbonyl and the consumption of isocyanate can be used for determination of residual isocyanate levels. FDEMS data collected showed that the addition of dibutyltin dilaurate catalyst in the 10% NCO system during polymerization at 40% relative humidity increased the initial cure reaction rate, and the time required for complete cure was reduced by nearly 240 minutes by the addition of the catalyst. Furthermore, FDEMS data suggest that increased residual isocyanate levels decrease cure rate within the bulk of uncatalyzed systems. The FDEMS and the FTIR cure data both suggest that the urea linkage hydrogen bonding was formed as a result of the vapor diffusion process. The FDEMS method for monitoring the moisture-curing reaction proved to be much more convenient and thereby more successful than FTIR.
because it allowed the capability of following the reaction with the sample on a horizontal plane as well as continuously and in-situ in the environment of a coating or in an adhesive bondline. A good correlation exists between the FDEMS changes in ionic mobility and the FTIR monitoring of the isocyanate during cure on the bulk of the 4% NCO system. Future integration of both test methods will lead to more quantitative results, additional studies on the reaction rates, and an understanding of adhesive properties as a function of the moisture diffusivity in the curing prepolymer. In addition, FDEMS measurements of deactivated systems such as alcohol addition at the reaction endpoint may lead to the determination of initial moisture diffusion rates in moisture-curing prepolymer systems.
Scheme 1. Prepolymer Curing Chemistry.

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<th>Sample #</th>
<th>% Residual NCO</th>
<th>Catalyst</th>
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</tr>
<tr>
<td>5</td>
<td>4.0 MeOH Deact.</td>
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Table 1. Isocyanate Prepolymers for FDEMS Measurements
Figure 1. *In-situ* IR plot showing the increase in the urethane carbonyl peak at 1724 cm\(^{-1}\) as the polymerization proceeds with time (80 °C nitrogen atmosphere, no catalyst, 4 % isocyanate)
Figure 2. *In-situ* IR plot showing the decrease in the NCO peak at 2272 cm\(^{-1}\) as the polymerization proceeds with time (80 °C nitrogen atmosphere, no catalyst, 4 % isocyanate)
Figure 3. IR absorbance peak profile showing relative growth rates for the N-H (1525 cm\(^{-1}\)) and Carbonyl (1724 cm\(^{-1}\)) peaks and simultaneous consumption of isocyanate at 2272 cm\(^{-1}\). After the initial 2.5-hour reaction, further growth and consumption resulted from urea formation due to controlled moisture ingress into the reaction flask.

Figure 4a. FDEMS of a 4% residual isocyanate prepolymer without catalyst over a range of frequencies (50, 25, 5, 0.5, 0.25, 0.125, 0.050 kHz; frequencies plotted highest to lowest, top to bottom) during cure.

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Figure 4b. FDEMS of a 4% residual isocyanate prepolymer with catalyst over a range of frequencies (50, 25, 5, 0.5, 0.25, 0.125, 0.050 kHz; frequencies plotted highest to lowest, top to bottom) during cure.

Figure 4c. FDEMS of a 10% residual isocyanate prepolymer without catalyst over a range of frequencies (50, 25, 5, 0.5, 0.25, 0.125, 0.050 kHz; frequencies plotted highest to lowest, top to bottom) during cure.
Figure 4d. FDEMS of a 10% residual isocyanate prepolymer with catalyst over a range of frequencies (50, 25, 5, 0.5, 0.25, 0.125, 0.050 kHz; frequencies plotted highest to lowest, top to bottom) during cure.

Figure 5a. FDEMS spectrum of a methanol deactivated isocyanate prepolymer exposed to 40% R.H. (Frequencies are 50, 25, 5, 0.5, 0.25, 0.125, 0.050 kHz; plotted highest to lowest, top to bottom)
Figure 5b. FDEMS spectrum of a methanol deactivated isocyanate prepolymer exposed to 40% R.H. (Frequencies are 0.050, 0.125, 0.25, 0.5, 5, 25, 50, 250, 500, 1000 kHz; plotted lowest to highest, top to bottom)

Figure 6. FTIR spectra showing the consumption of the isocyanate peak during cure at 2272 cm⁻¹ (40 % RH, 25 °C, 4 % isocyanate in the absence of catalyst).

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Figure 7. Direct comparison between the rates of urethane prepolymer cure monitored using FTIR and FDEMS at 500 Hz under similar environmental conditions (40 % RH, 25 °C. 4 % isocyanate in the absence of catalyst).
References for Chapter 5


Chapter 6: Conclusions

The investigations in the previous three chapters have demonstrated the usefulness of:

- Size Exclusion Chromatography with Multi Angle Laser Light Scattering detection to characterize the state of a new polymer, Poly(N-methyl perfluorooctyl sulfonamido ethyl acrylate).

- Size Exclusion Chromatography with Multi Angle Laser Light Scattering detection to characterize the aging of PA-11 in aqueous aging environments.

- Frequency Dependent Electromagnetic Sensing to monitor the changing state and moisture content of an adhesive during cure.

Specific conclusions of the three studies include:

1) Multi Angle Laser Light Scattering was proven to be a reliable and accurate technique for measuring molecular size and molecular weight for a new polymer system with a complicated structure and unknown characteristics. The inability of the Viscosity - Right Angle Laser Light Scattering approach to characterize this polymer system, due to the assumptions and conditions necessary for the technique to work, is strong evidence that the accuracy of this widely accepted and used Viscosity-RALLS technique needs to be re-evaluated. A strong case has been presented for the validity of the MALLS approach, explaining why the technique is rapidly becoming the standard for macromolecular characterization.
2) The SEC-MALLS technique effectively monitored the changing molecular weight of PA-11 aging in a pH7 water environment. A mathematical model successfully fit the molecular weight data and was used to determine the activation energy of amide hydrolysis-degradation reaction in the aging environment. More importantly, it was determined that an equilibrium molecular weight is approached during PA-11 aging in pH7 water. Conclusive evidence was found that a competing recombination reaction exists which gives rise to this equilibrium condition. The discovery of this recombination reaction opens the possibility of an indefinitely healthy PA-11 material.

3) FDEMS is proven to be an optimal technique for monitoring changing water content and degree of cure in a moisture-curing adhesive. FDEMS is capable of convenient, continuous in situ molecular measurements which are inaccessible to other monitoring techniques. The data show potential for total cure characterization by FDEMS, including in situ determinations of moisture diffusion rates into a polymer cure bondline, a determination which has not been achievable before this research.

Accurate and reliable techniques such as MALLS and FDEMS make possible the identification of conditions which lead to a material’s failure and characterization of degradation, as seen in the PA-11 study, as well as monitoring of the changing state of a material in situ during cure and use. Ultimate development and application of these techniques will lead to prevention of disasters due to material failure, and unsurpassed material quality control via a perfectly non-destructive and in situ technique.
VITA

Andrew Orschel Meyer


Upon graduation the author will embark on a career as an Applications Chemist at Wyatt Technology Corp., Santa Barbara, CA.