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Molecular Weight Measurement of Biobased Furan Polyamides via Non-Aqueous Potentiometric Titration

by LaShonda T. Cureton, George Fountzoulas, and John J. La Scala

ARL-TR-6490 **June 2013**

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REPORT DOCUMENTATION PAGE

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OMB No. 0704-0188

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
June 2013	Final	July 2012

4. TITLE AND SUBTITLE
Molecular Weight Measurement of Biobased Furan Polyamides via Non-Aqueous Potentiometric Titration

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
LaShonda T. Cureton,* George Fountzoulas, and John J. La Scala

5d. PROJECT NUMBER
MMB104

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: RDRL-WMM-C
Aberdeen Proving Ground, MD 21005-5069

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-6490

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
*Oakridge Institute for Science and Education , Oak Ridge Association of Universities, P.O. Box 117, Oak Ridge, TN 37831-0117

14. ABSTRACT
The U.S. Department of Defense (DOD) has increased the use of polymers due to their lightweight nature and high performance in composite materials, body armor, and military vehicles. Unfortunately, traditional polymers are petroleum-derived, thus creating supply chain vulnerability. The DOD is looking to replace these petroleum-based polymers with less costly and more "eco-friendly" alternatives. This research seeks to develop furan-based polymers as biobased alternatives to nylon, Nomex, Kevlar, and other high-performance polyamides. U.S. Army Research Laboratory researchers have synthesized bio-/furan-based polyamides. Characterizations of these polymers are difficult because of their insolubility in most solvents. This work examines the use of potentiometric titration to measure the concentration of amine and carboxylic acid groups to enable measurement of the number-average molecular weight of these polymers. The method was established by conducting a series of sample titrations using the monomers and 1,6-hexamethylenediamine; succinic acid; 2,5-furandicarboxylic acid; and adipic acid (0.100 g) in various solvents.

15. SUBJECT TERMS
titration, biobased, furan, polyamides, monomers

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					John J. La Scala
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (*Include area code*)
Unclassified	Unclassified	Unclassified	UU	34	410-306-0687

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

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1. Introduction

The Department of Defense (DOD) uses high-performance composites and polymers in a host of applications. The development of high-performance polymers and composites from environmentally friendly resources has garnered much attention in recent years due to environmental concerns, the unstable rise in petroleum oil prices, and, most notably, the increased demand of petroleum (*1*). The increasing demand of oil is not due solely to U.S. needs; developing industrial countries such as India and China (figure 1) have contributed greatly (*2*). Several solutions have been proposed to account for the increased demand of petroleum. One notable proposal suggests that the United States increase its own oil production (*3*). However, increasing oil production would not be time and cost efficient, as it would take around 10 years to set up new oil operations and another 20 years to obtain peak oil production. Even at peak production, oil prices would drop only by $0.75 per barrel (*3*). Analysts have predicted that around the year 2040 our petroleum-based energy economy will be phasing out (figure 2), and it will be more economically competitive to use renewable materials than petroleum (*4*). The more reasonable approach would be to reduce our dependency on petroleum by encouraging research and manufacture of renewable resources (*4*).

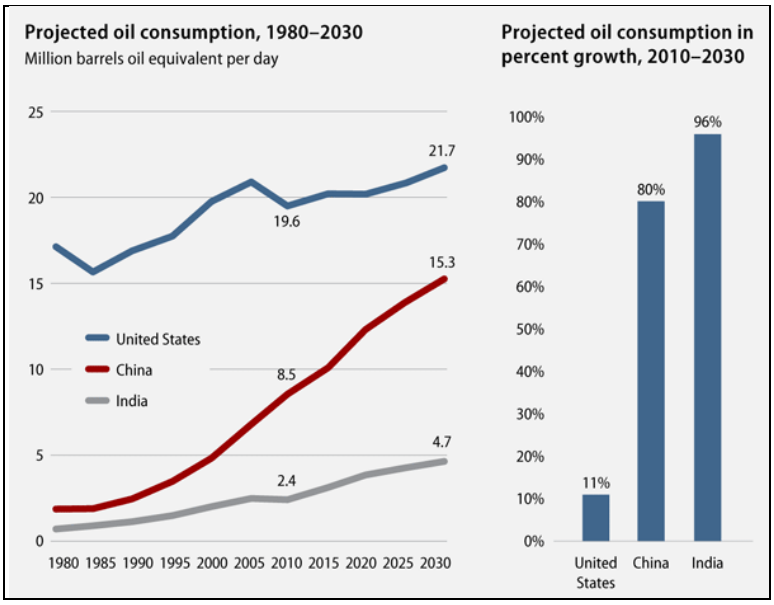

Figure 1. Oil consumption for the United States, China, and India (*2*).

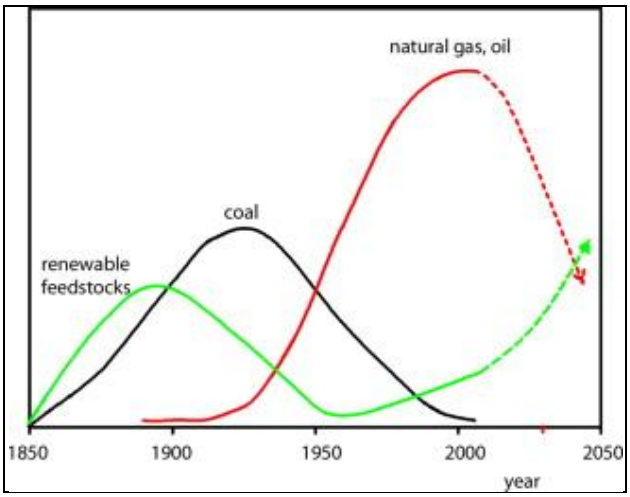

Figure 2. Historical perspective of raw materials (*4*).

The DOD has initiated programs and compliance requirements such as the Green Procurement Program (*5*), Reduce/Eliminate Pollution for Compliant Composite Manufacturing and Repair, and the Army Environmental Requirements and Technology Assessments. These programs are designed to facilitate development of "green" materials and high-performance polymers and reduce the amount of hazardous waste from the manufacturing process. To fulfill the goal of reducing hazardous waste and producing high-performance materials from "green" materials, any proposed green or biobased alternatives to petroleum-based materials must meet several basic requirements before they can be used for high-performance materials and composites. The biobased precursors must be obtainable in large quantities in a consistent quality from renewable feedstocks, reasonably priced on the market, reactive in diverse reactions (*6*), and, most important to the DOD, have properties that can be maintained in highly stressful environments, such as solid rocket boosters or aviation and military structures (*7*).

Current DOD research seeks to develop biobased alternatives to nylon, Nomex, Kevlar, and other high-performance polymers. To obtain comparable properties, we sought to develop furan-based polyamides. Furan is a heterocyclic organic compound, consisting of a five-member aromatic ring with four carbon atoms and one oxygen atom. Furan has been investigated in chemistry syntheses for specialty chemicals and polymers (*8, 9*). Furan is an attractive compound because it is chemically obtainable through the modification of glucose. Glucose can be modified through a series of catalytic oxidation or hydrogenation processes to produce furan derivatives with several functionalities (figure 3) (*10*). The major source of glucose is in plant products like corn, which is an abundant renewable resource. The United States produced approximately 320 million tons of corn from 2010 to 2011 (*11*), a sufficient amount to ensure the availability of furan and many derivatives for large- and small-scale resins and polymers.

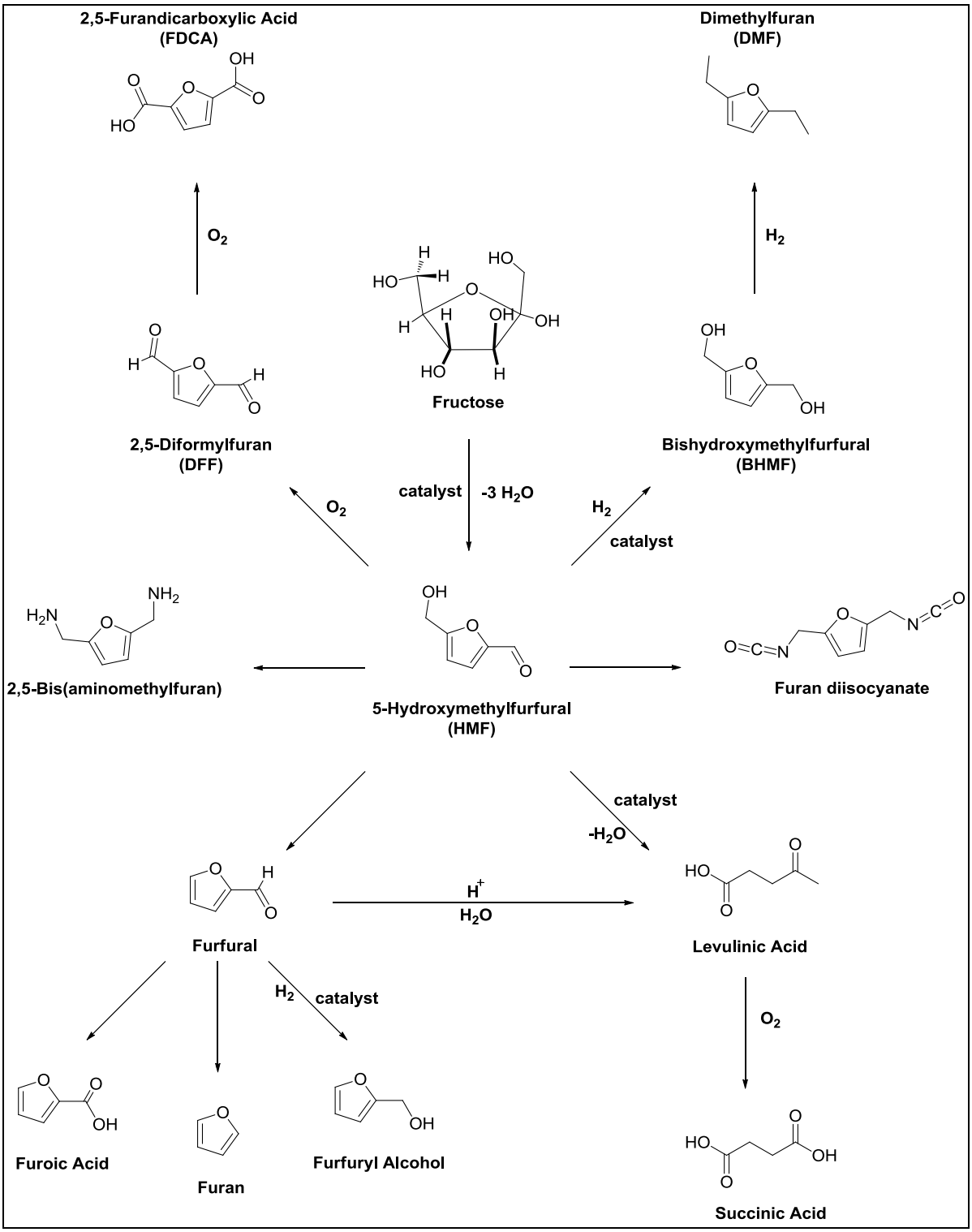

Figure 3. Synthetic routes for development of furan derivatives.

For step-growth polymers, like polyamides, end groups can consist of the reactive end group of either or both monomers. In the case of polyamides, amine end groups will be present if an excess of diamine is used in the polymerization, while the end groups would be carboxylic acids if synthesized with an excess of diacid. Additionally, the polyamide can also have a mix of the two end groups, acid and amine. This typically occurs when stoichiometry is nearly balanced or if diffusion limitations severely reduce the polymerization rate. In all cases, the end groups can be quantified and the number-average molecular weight, M_n, of the polymer can be determined through titration, which is one method to quantify the end groups. Polymers such as nylon and biobased furan polyamides are not soluble in aqueous solutions and must be titrated through a non-aqueous potentiometric titration. Unlike aqueous titrations that use a visible indicator to indicate the titration end point, non-aqueous titrations measure transitions in electrochemical potential. Non-aqueous potentiometric titration can be a better measure of molecular weight than light scattering or chromatographic methods for rigid non-random walk polymers (*12*). Non-aqueous potentiometric titration has been well established in the literature and frequently used for a host of polymers (*13, 14*). Considering the high level of expected rigidity for furan-based polymers that limit the accuracy of other molecular weight measurements, it important to assess non-aqueous potentiometric titration for molecular weight measurements of these polymers.

With non-aqueous potentiometric titration, a sample is dissolved in the non-aqueous solvent (a polar or nonpolar solvent) and titrated with a concentrated solution of acid or base depending on the test. The titration process is monitored via a glass and reference electrode (or a combination electrode; a pH meter can also be used). The potential difference is plotted against the volume of titrant, and an end point is determined from averaging the points in the inflection of the resulting titration curve. Using a series of calculations, the M_n of a sample is determined. Non-aqueous potentiometic titration is a relatively quick and proven technique providing more accurate results than other methods for determining M_n through end group analysis.

This work examines the use of non-aqueous potentiometric titrations to measure the concentration of amine and acid groups to calculate the number-average molecular weight of the titration of biobased furan polyamides. The biobased furan polyamides that will be investigated in this report are poly(butylmethylene furanamide) and poly(hexamethylene furanamide) in addition to the monomers that constitute these polymers and model compounds to test the methodology.

2. Materials and Experimental Procedures

2.1 Synthesis of Furan-Based Polyamides

Shown in figure 4, the biobased furan polyamides, poly(butylmethylene furanamide) and poly(hexamethylene furanamide), were prepared through interfacial polymerization from 2,5-furandicarboxylic acid chloride (A) with varying chain-length aliphatic diamines (B), in this case, 1,6-hexamethylene diamine or 1,4-diaminobutane. Interfacial polymerization is the process in which the synthesis takes place in the interface between the organic phase (chloroform) and the aqueous phase (15 wt% NaOH solution). Tetrabutylammonium bromide (TBAB) is used as a phase transfer agent to keep the polymer in the organic phase during polymerization (*15*). The entire polymerization process normally takes 15 h. The solid polymer was filtered and thoroughly washed with water (200 mL) and acetone (100 mL). The biobased furan polyamides were filtered and dried under vacuum at 105–120 °C.

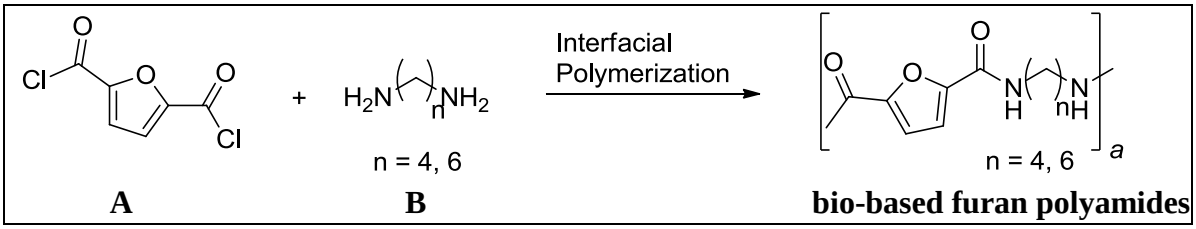

Figure 4. Synthetic route for biobased furan polyamides.

2.2 Potentiometric Titration

A Keithley Electrometer (Model 610B) and a double-junction glass-bodied combination pH electrode (Oakton WD-3580-04) were used to measure potential differences of various solutions. A Hirschmann Solarus Electronic Burette was used to titrate the non-aqueous amine solutions and a 25-mL glass burrette was used to titrate the non-aqueous acid solutions. Due to the electrode sensitivity to the surrounding electromagnetic fields, all titrations were completed in a chemical hood, which acted as a Faraday cage (a shield used to blocks external static and nonstatic electric fields).

A series of non-aqueous potentiometric titrations was conducted on the monomers: 1,6-hexamethylenediamine, 1,4-diaminobutane, succinic acid, adipic acid, and 2,5-furandicarboxylic acid. Once optimized for the monomers, the potentiometric titrations were performed on the poly(butylmethylene furanamide) and poly(hexamethylene furanamide). The solvents used in this study were glacial acetic acid, isopropyl alcohol dimethyl sulfoxide (DMSO), and dimethylformamide (DMF), which provide a baseline for extrapolation. Poly(butylmethylene furanamide) and poly(hexamethylene furanamide) were dissolved in DMFand titrated with 0.1-*N* perchloric acid in acetic acid and 0.1-*M* potassium hydroxide in isopropyl alcohol to measure the concentration of amine and acid groups, respectively.

2.3 Materials

Perchloric acid, standard solution in acetic acid (0.1 *N*), 1,4-diaminobutane, 1,6-hexamethylenediamine, adipic acid, succinic acid, potassium, hydrogen phthalate, concentrated hydrochloric acid, and pH buffer solutions were purchased from Sigma-Aldrich. DMF was purchased from Alfa Aesar. Phenolphthalein indicator was purchased from Ricca Chemical Company. Lithium chloride was purchased from OmniPurr. The 2,5-furandicarboxylic acid was purchased from AK Scientific Inc. Potassium hydroxide was purchased from EMD Chemical Inc. All chemicals and reagents were used as received.

2.4 Experimental

2.4.1 Non-Aqueous Potentiometric Titration of Amine With Perchloric Acid, Standard Solution in Acetic Acid, (0.1 *N*)

Amine titration measured the amount of perchloric acid (milliliters) needed to titrate a sample amine (1 g) in solvent to an end point. The procedure used for titration of amines was from the ASTM D 2896-05 Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration (Procedure B) (*16*). Titration measurements were completed for: blank solvents, glacial acetic acid, DMSO/glacial acetic acid mixture, and DMF; the monomer 1,6-hexamethylene diamine; and the biobased furan polyamides, poly(butylmethylene furanamide) and poly(hexamethylene furanamide).

2.4.1.1 Potentiometric Titration of the Blank Solution

Glacial acetic acid (50 mL) was added to a 250-mL container equipped with a magnetic stirring bar. The blank solution was titrated with 0.1-*N* perchloric acid solution and the potential difference was measured and recorded. This procedure was used for the titration of chlorobenzene, DMF, DMSO, and mixtures of glacial acetic acid with chlorobenzene, DMSO, and DMF solvents using the same procedure.

2.4.1.2 Potentiometric Titration of the Monomer

1,6-Hexamtheylenediamine (0.06 g) was added to a 250-mL container with 50 mL of glacial acetic acid and a magnetic stirring bar. The diamine solution was titrated to a minimum of 25 mL in increments of 0.5 mL with 0.1-*N* perchloric acid solution from an electronic burette, and the potential difference was measured and recorded. The monomer (0.15 g) was also titrated in DMF and mixtures of glacial acetic acid with chlorobenzene, DMSO, and DMF solvents using the same procedure.

2.4.1.3 Potentiometric Titration of the Biobased Furan Polyamides

Furan polyamide, poly(hexamethylene furanamide) (0.104 g), was added to a 250-mL container with 25 mL of DMF and a magnetic stirring bar. The diamine solution was titrated to a minimum of 25 mL in increments of 0.2 mL with 0.1-*N* perchloric acid solution from an

electronic burette, and the potential difference was measured and recorded. This procedure was also used for the titration of poly(butylmethylene furanamide) (0.097 g).

2.4.1.4 Equations for Nonaqueous Potentiometric Titration of Amine With Perchloric Acid

The end point of the titration can be used to calculate the experimental base number (EBN) of the biobased furan polyamides and compared to the theoretical base number (TBN), which is the actual number of amine end groups the polyamide should have based on the molar mass of the monomer. ASTM D 2896-05 (*16*) expresses base number in terms of milligrams of potassium hydroxide (KOH) per gram of sample. The equation for the $M_{n,\,NH2}$ is a variation of the EBN; however, it does not incorporate the molar mass of the amine end group.

$$N = \frac{32.06*1000}{monomer_{molar\ mass}}\ . \tag{1}$$

Molar mass of one and two amine end groups is 16.03 g/mol and 32.06 g/mol, respectively.

$$EBN = \frac{(E-F)*C*16.03}{S}\ , \tag{2}$$

where

E = $HClO_4$ solution used to titrate the sample to the end point of the titration curve, mL,

F = volume (correction factor) corresponding to E for blank titration at same potential as sample, mL,

C = concentration of $HClO_4$ solution, and

S = mass of sample in solution, g.

$$M_{n,\,NH_2} = 2(\frac{S}{(E-F)*C}), \tag{3}$$

where

$M_{n,\,NH_2}$ = molecular weight, g/mol,

S = mass of sample in solution, g,

E = volume of titrant, L,

F = volume of the blank, L, and

C = concentration of titrant, mol/L.

2.4.2 Non-Aqueous Potentiometric Titration of Acid With Potassium Hydroxide, Standard Solution in Isopropyl Alcohol, (0.1 *M*) (*11*)

Acid titration measured the amount of potassium hydroxide (milliliters) needed to titrate a sample acid (1 g) in solvent to an inflection. The procedure used for titration of acid was from ASTM D 664-11a, Procedure B (*17*). Tests were completed for: blank solvents, isopropyl alcohol, and DMF; the monomer 1,6-hexamethylene diamine; and the biobased furan polyamides, poly(butylmethylene furanamide) and poly(hexamethylene furanamide).

2.4.2.1 Standardization of the Titrant Potassium Hydroxide Solution

Deionized (DI) water (400 mL) was gently boiled for 5 min to remove CO_2. Potassium hydrogen phosphate (KHP) (0.064 g) was added to 100 mL of the cooling DI water in a glass beaker. After the solution cooled completely, four drops of phenolphthalein indicator and a magnetic stirring bar were added to the beaker. The KHP solution was titrated with the KOH standard solution in increments of 0.2 mL using a glass burrette. The voltage of each increment was recorded and the titration ended 6 mL after the end point was detected. Standardization of the KOH standard solution was calculated using equation 4 and calculated to be 0.0066 *M* (6.6 *mM*).

$$\frac{KHP_{grams}}{KHP_{molecular\ weight}} = KHP_{moles}\ ,$$

$$KHP_{moles} = KOH_{moles}\ , \tag{4}$$

and

$$\frac{KOH_{moles}}{Liters_{titrated}} = Concentration\ of\ KOH\ Solution.$$

2.4.2.2 Potentiometric Titration of the Blank Solution

Isopropyl alcohol (50 mL) was added to a 250-mL container equipped with a magnetic stirring bar. The blank solution was titrated in increments of 0.2 mL with 6.6-*mM* KOH solution using a glass burrette, and the potential difference was measured and recorded. This procedure was used for the titration of DMF solvent.

2.4.2.3 Potentiometric Titration of Monomer

Adipic acid (0.1 g) was added to a 250-mL beaker containing a magnetic stirring bar and 25 mL of isopropyl alcohol. The acid solution was titrated to a minimum of 20 mL in increments of 0.2 mL with 6.6 *mM* KOH solution using a glass burrette, and the potential difference was measured and recorded. This procedure was used for the titration of monomers, succinic acid (0.1035 g), 2,5-furandicarboxylic acid (0.1002 g), and adipic acid (0.100 g) in DMF solvent.

2.4.2.4 Potentiometric Titration of the Biobased Furan Polyamides

Furan polyamide, poly(hexamethylene furanamide) (0.097 g), was added to 25 mL of DMF in a 250-mL container equipped with a magnetic stirring bar. The diamine solution was titrated to a minimum of 25 mL in increments of 0.5 mL with 6.6-*mM* KOH solution from a glass burrette, and the potential difference was measured and recorded. This procedure was also used for the titration of poly(butylmethylene furanamide) (0.103 g).

2.4.2.5 Equations for Non-Aqueous Potentiometric Titration of Acid With KOH

In the following series of equations, the end point of the titration can be used to calculate the experimental acid number (EAN) of the biobased furan polyamides and compared to the theoretical acid number (TAN), which is the actual number of acid end groups the polyamide should have based on the molar mass of the monomer. ASTM D 664-11a (*17*) expresses the AN in terms of milligrams of KOH per gram of sample. The equation for the $M_{n,\,OH}$ is variation of the EAN; however, it does not incorporate the molar mass of the acid end group, 90.04 g/mol.

$$TAN = \frac{45.02*1000}{monomer_{molar\ mass}}. \tag{5}$$

Molar mass of one and two carboxylic acid end groups are 45.02 and 90.04 g/mol, respectively.

$$EAN = \frac{(E-F)*C*90.04}{S}, \tag{6}$$

where

E = KOH solution used to titrate the sample to the end point of the titration curve, mL,

F = volume (correction factor) corresponding to E for blank titration at same potential as sample, mL,

C = concentration of KOH solution, and

S = mass of sample, g.

$$M_{n,COOH} = 2\left(\frac{S}{(E-F)*C}\right), \tag{7}$$

where

$M_{n,\,COOH}$ = molecular weight,

S = mass of sample, g,

E = volume of titrant, L,

F = volume (correction factor) of the blank, L, and

C = concentration of titrant, mol/L.

2.5 Model Titration Curve for Understanding Polyamide Titrations

Figure 5 exemplifies titration curves that can be produced in this study. There are two cases that can be present in this study, calculating the base number (BN) or the acid number (AN) of a sample with a correction factor or without a correction factor. The correction factor is the adjustment made to the calculation of the samples to account for deviations in the sample solution. A blank solution is titrated to an inflection where the end point is determined; the end point, F, is the correction factor. If the blank does produce an inflection, then $F = 0$. If the blank does have an inflection, F is used as a correction factor in the BN, the AN, or the M_n calculations. E is the end point determined from the volume needed to titrate a sample to an inflection.

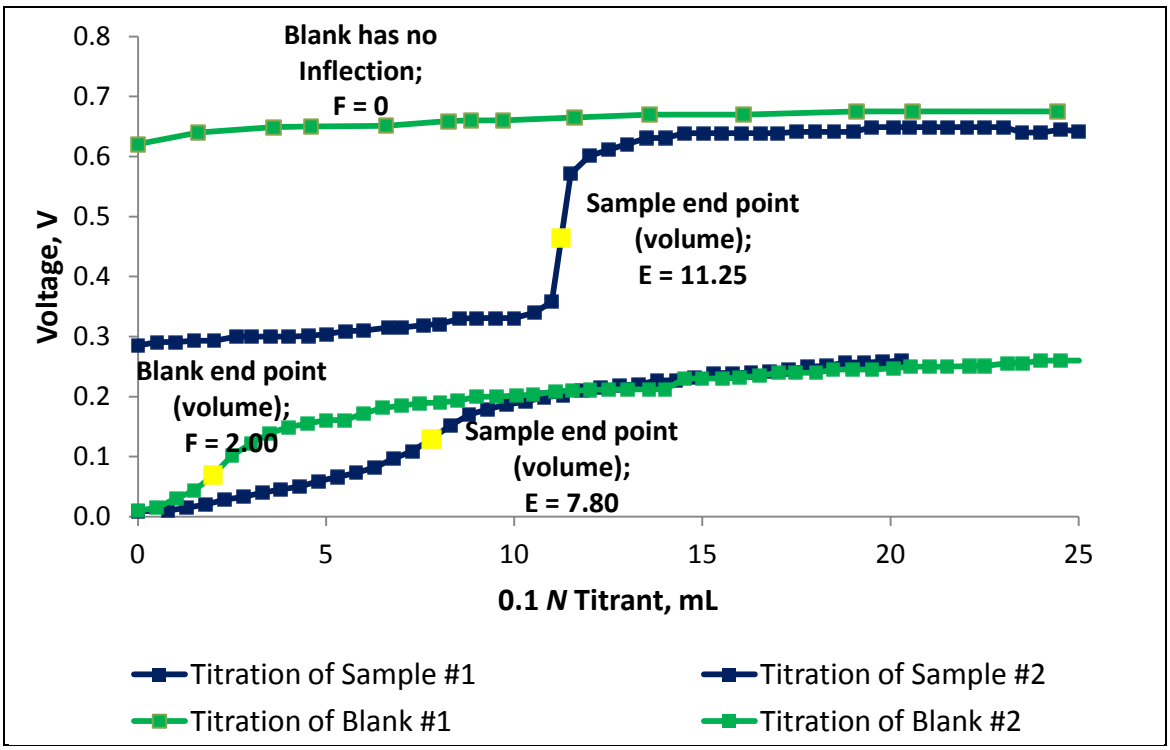

Figure 5. Model titration curves for blanks and samples.

2.6 Size Exclusion Chromatography (SEC)

The SEC system used in this study was a Waters system composed of a Waters 717 plus Autosampler held at 40 °C, Waters 510 Pump, and Waters 410 Refractive Index Detector held at 40 °C. Two columns (300 × 7.6 mm) held at 40 °C were used to separate molecular weights: Phenogel 5µ 10^4 Å and Phenogel 5µ 500Å. The solvent used was helium-purged DMF with LiCl salt at 0.06 M, pumped at 1 mL/min. The relative molecular weights of the polyamides were determined by calibration with polystyrene narrow molecular weight standards. There was a mix of four standards in DMF with 0.06 M LiCL: 51,000, 20,400, 5050, and 580 amu. Standard 580 amu had to be rejected from calculations due to blockage by the solvent front. Because this

molecular weight is far outside the desired molecular weights for the polyamides, there was little concern with rejecting this standard. This standard mix was injected (50 μL) every four unknown injections and then compared. Results were satisfactory for the analysis (R^2= 0.998). The furan polyamide samples were prepared by dissolving them in DMF with LiCl salt and then filtering them using PTFE syringe filters. All sample concentrations were approximately 1 g/L. Injection volume was 50 μL.

2.7 Nuclear Magnetic Spectroscopy (NMR)

^1H NMR spectra were obtained using a Bruker 600-MHz spectrometer at 25 °C. Spectra for the monomers were obtained in a 0.1%–0.5% deuterated methanol solution and the polymers were obtained in a 0.1%–0.5% deuterated DMF solution.

3. Results and Discussion

ASTM D 2896-05 (*16*) and D 664-11a (*17*) were standard test methods for measuring the BN and AN, respectively, of petroleum products. In this work, procedure B of the standards were used as a reference for conducting the titration experiments toward calculating BN and AN for the biobased furan polyamides to obtain molecular weight. While procedure A produced reasonably reproducible and repeatable titration curves in non-aqueous solvents, procedure B was used because a lower sample size, a maximum of 10 g as opposed to 20 g, could be used. The sample size used in these titrations afforded higher sample concentrations because less solvent was used in procedure B, i.e., 60 mL as opposed to 120 mL in procedure A. Otherwise, both procedures are the same—the titrant (0.1 *N* $HClO_4$), titration solvent (chlorobenzene), and instrumental setup.

The titration curves represent potentiometric titrations of amine followed by titrations of acid. For both sets of potentiometric titrations, titrations of solvent blanks were performed and the measurements were used as correction factors in the calculation of the BN and AN of the furan nylon samples. The BN/AN of the monomers was measured to establish a proof of concept of the standard test methods. The titration curves of the solvent blanks, monomers, and the subsequent polymers are shown in figures 5–12. The curves were examined for an inflection in which an end point can be determined. The inflection is indicating the smallest amount of titrant added that is sufficient to fully neutralize the analyte.

3.1 Amine Titration

The biobased furan polyamides are not soluble in chlorobenze (table 1), which is the solvent of choice in ASTM D 2896-05 for BN potentiometric titration. Therefore, a goal of this experimental work was to identify solvents that dissolve the polymer and allow for accurate molecular weight measurement through potentiometric titration. A series of solvent blank

titrations were conducted in glacial acetic acid, chlorobenzene, DMF, DMSO, and mixtures of glacial acetic acid with chlorobenzene, DMSO, and DMF. The 0.1-*N* perchloric acid in acetic acid solution, a strong acidic solution, was used as the titrant. The blanks were measured to ensure that the solvent in the solution used did not contribute to the overall titration measurements. Glacial acetic, particularly, was used per ASTM D2896-05 to help improve solubility of the basic samples in non-aqueous solvents and is a commonly used titration solvent to provide distinct potential curves with clear end points (*18*).

Table 1. Solvent properties and solubility.

Solvent	**Dielectric Constant, ε, (*19*)**	**Type of Solvent**	**1,6-HMDA**	**Adipic Acid**	**Polyamide**
Chlorobenzene	5.62	Nonpolar	+	—	—
Acetic acid	6.20	Polar protic	+	+	—
Isopropyl alcohol	20.18	Polar protic	+	+	—
DMF	38.25	Polar aprotic	+	+	+
DMSO	47.24	Polar aprotic	+	+	+

Notes: + = soluble at RT; — = insoluble at RT.

The titrations showed differing potential curves, as illustrated in figure 6. Glacial acetic acid reflected a steady positive potential with no inflection. This could be related to the subtle change in pH as it relates to the titrant and the blank solution. Acetic acid has a pH of 2.4 and perchloric acid in glacial acetic acid has a pH of <1, which means there a very small change in the pH and thus a small change in potential difference to be observed. Similarly, the titration curves of chlorobenzene and DMSO increased within the first 1 to 2 mL and then leveled off to a consistent voltage at 25 mL. However, for DMF, the titration curve was logarithmic, yielding a negative potential. Table 1 lists the solvent properties of the solvents in this study; there are major differences in polarity and the dielectric properties of DMF and acetic acid. Two situations could be taking place in the titration of DMF blank: (1) hydrolysis by the presence of a strong acid (perchloric acid) to form formic acid and dimethylamine (*20*) or (2) the lack of solvation of the anions in solution. In the first case, the pH difference would not be significant enough to invoke a potential difference. However, no indication of hydrolysis took place. The lack of solvation would be due to the difference in the dielectric constants. During titration, the ions are not solvated to initiate a potential difference. Using DMF as solvent for dissolving the polymers would affect potential difference (a negative value) when titrating with the strong acid.

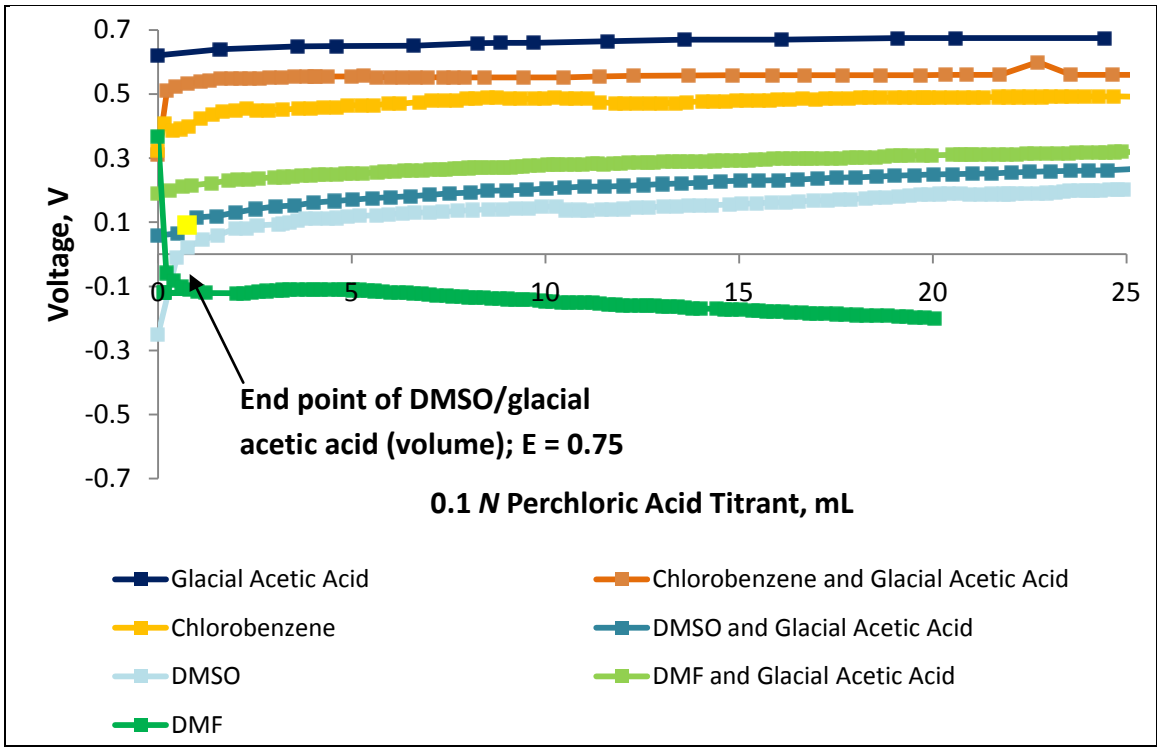

Figure 6. Amine titrations of the blanks.

Titrations were also done on solvent mixtures with glacial acetic acid to establish a thorough evaluation of the blanks and solvent interactions. Chlorobenzene/glacial acetic acid mixture was very inhomogeneous, as the solvents are of different polarities (table 1). Despite the inhomogeneuity, through the titration, the titration curve had a consistent voltage (0.55999 V) lying between glacial acetic acid and chlorobenzene blanks. DMSO/glacial acetic acid mixture produced a logarithmic curve with a 0.75-mL (0.09-V) end point before the curve leveled off. This inflection was used as *F* (correction factor) in all calculations using the DMSO/glacial acetic acid blank. The DMF/glacial acetic acid mixture displayed a titration curve different from that of the DMF blank. The curve was positive and closely resembles glacial acetic acid of a lower voltage measurement. Titration of the mixtures showed consistent results; they all fell between glacial acetic acid and the solvent with no inflection other than DMSO/glacial acetic acid.

The TBN of 1,6-hexamethylenediamine is 275.90 mg/g, as determined by equation 2, and the molar mass of the monomer is 116.2 g/mol. These values were compared to the EBN determined by equation 3 and the $M_{n,\,NH2}$ calculated using equation 4 in the various solvents. Figure 7 shows the titration of 1,6-hexamethylenediamine monomer in various solvents. For these samples, inflections were observed and the end points are indicated by a yellow mark at the center of the inflection of the titration curves.

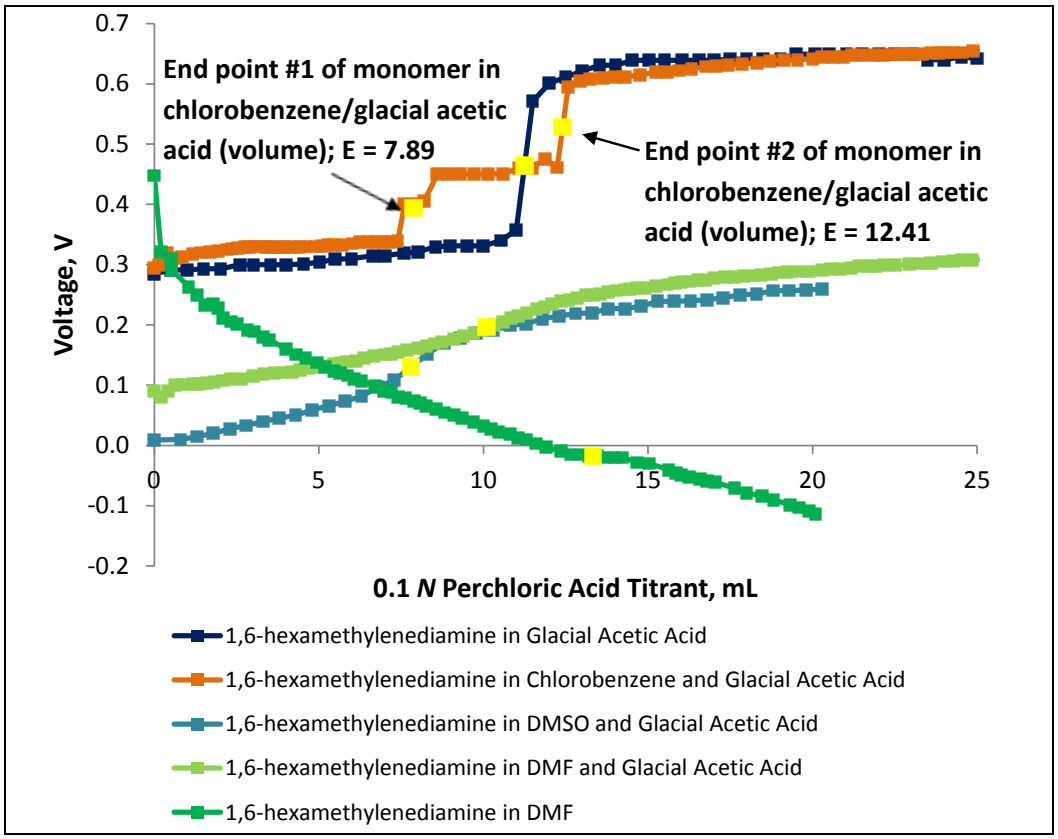

Figure 7. Amine titrations of 1,6-hexamethylenediamine in various solvents.

Titration of the monomer in glacial acetic acid showed a distinct sigmoidal curve with an end point at 11.25 mL. The EBN and $M_{n,\,NH2}$ for the monomer in glacial acetic acid were calculated without using the glacial acetic acid blank as a correction factor (F in equations 2 and 3) because the titration curve of the glacial acetic acid blank was a linear plot with no inflection and overlays the monomer titration curve.

Not as distinctly defined as the monomer/glacial acetic acid titration, the titration of the monomer in DMSO/glacial acetic acid mixture had a broad sigmoidal curve with an end point at 7.80 mL. The EBN and the $M_{n,\,NH2}$ for the monomer in DMSO/glacial acetic acid mixture were calculated two ways. The first calculation was done using the blank as a correction factor because a minor inflection was shown in the DMSO/glacial acetic acid blank (around 0–0.15 V), and it is important to adjust the calculation. The second was done without using the correction factor to determine whether the variation would be a significant factor in calculating the EBN and the $M_{n,\,NH_2}$ or whether using the correction factor provides a more accurate measurement.

Titration of 1,6-hexamethylenediamine monomer was also conducted in chlorobenzene/glacial acetic acid and DMF/glacial acetic acid mixtures. In chlorobenzene/glacial acetic acid mixture, two inflections were observed, indicative of the inhomogeneuity and the preference of the monomer solubility in glacial acetic acid. Based on the solution properties observed at 6.75–8.0 mL, the first inflection is likely that of the emulsion, in which monomer/glacial acetic acid solution is unequally dispersed. The second inflection is a keen reflection of the monomer titration in glacial acetic acid, as it is very close to that of the monomer glacial acetic acid titration. Here, solid precipitation from the solution is observed at 11.09 and 12.24 mL; the needle on the voltmeter "jumped," which likely signaled the onset of inflection.

Titration of 1,6-hexamethylenediamine were also done in DMF/glacial acetic acid mixture and in DMF. The titration curve for 1,6-hexamethylenediamine in DMF/glacial acetic acid exhibited a broad sigmoidal curve like the DMSO/glacial acetic acid result, but with a higher end point at 10.10 mL. Opposite this result, titration in DMF yielded a completely different curve from the previous solvents (figure 7). The curve tapers down to negative potential values, resulting in a negative sigmoidal curve. It is important to acknowledge that 1,6-hexamethylenediamine was only slightly soluble in DMF, and the monomer only showed solubility after approximately 4.0 mL of titrant was added to the DMF solution. This insolubility would be one reason why no inflection is observed while the curve is positive. It is likely that only until the monomer is soluble in acetic acid that a change in potential is observed, though not enough to shift the curve in the positive direction. The results further confirm that the lack of solvation of the ion pairs in DMF solution will affect the potential difference (a negative value) when titrating with the strong acid. Since DMF was used without a co-solvent like glacial acetic acid, negative potential values (below 0 V) would be observed during the titration. Despite solubility, another notion for this observation is that DMF is a polar aprotic solvent with a moderate dielectric constant and will likely have no solvating power for dissociating $–NH_2$ anions formed in solution. Regardless of this fact, an end point for the titration was observed at about 13 mL (and –0.02 V), and EBN and the $M_{n,\,NH}$ were calculated without using the blank as a correction factor. It is wise to conclude the titration of the polymers in DMF will likely yield negative potential values creating analogous titration curves to the blank and monomer in DMF.

The data from these amine titrations are outlined in table 2. Titration of 1,6-hexamethylenediamine in glacial acetic acid mixture yielded an EBN of 224 mg/g and a $M_{n,\,NH2}$ of 143 g/mol. Similar to these results, the second end point from the titration of 1,6-hexamethylenediamine in chlorobenzene/glacial acetic acid mixture yielded an EBN of 278 mg/g, which is closer to the TBN (275.90 mg/g) than all of the values obtained from the other titrations. Also, the $M_{n,\,NH2}$ (115 g/mol) calculated from this titration is within 1% error of the known molecular weight of 1,6-hexamethylenediamine. From the latter results, it is likely the titration was another attempt at titrating 1,6-hexamethylenediamine in glacial acetic acid. Upon addition of 0.1-*N* perchloric acid in acetic acid, the monomer was becoming more soluble in glacial acetic acid and the amount of chlorobenzene had less of an effect on the solution properties (i.e., emulsion

formation). Again, the first end point of this titration is an obvious titration of the dispersed monomer and glacial acetic acid solution, which is why the percent errors for EBN and $M_{n,\ NH2}$ are highest for the solvent/glacial acetic acid mixture titrations.

Table 2. Amine titration of 1,6-hexamethylenediamine.

Solvent	**EBN (mg/g)**	**% Error**	$M_{n,\ NH_2}$ **(g/mol)**	**% Error**
Glacial acetic acid	224	19	143	23
DMSO/glacial acetic acid	—	—	—	—
with *F* (correction factor)	155	44	207	78
without *F* (correction factor)	204	26	157	35
Chlorobenzene/glacial acetic acid	—	—	—	—
End point no. 1	177	36	181	56
End point no. 2	278	1	115	1
DMF/glacial acetic acid	230	17	139	20
DMF	142	48	225	94

The 1,6-hexamethylenediamine in DMSO/glacial acetic acid and DMF/glacial acetic acid mixtures produced similar results, as indicated by their nearly identical sigmodial curves. Using the blank DMSO/glacial acetic acid mixture as an *F* (correction factor) did not help improve the calculation of the EBN and the $M_{n,\ NH2}$; in fact, use of the correction factor made the percent error significantly higher. In this case, the inflection identified is not an actual representation of the blank titration.

The last result is the monomer in DMF titration. This titration resulted in a 142-mg/g EBN, which is a 48% error of the TBN. Additionally, calculation of the $M_{n,\ NH2}$ produced a value twice the molecular weight of 1,6-hexamethylenediamine. These results indicate that DMF is not an ideal solvent to use for amine of titration.

Titration of 1,6-hexamethylenediamine in glacial acetic acid is a perfect example of the kind of titration curve the monomers and polymers should produce. The curve is sigmoidal and produces an inflection, which can be used to calculate EBN and $M_{n,\ NH2}$. In addition, the titration of the blank shows no inflection and would not be required for correction. In this case, glacial acetic acid would be an ideal solvent to use for the titration of the polymers; however, the polymers in this study were soluble only in DMSO and DMF. Initial attempts to measure the EBN and Mn, NH2 of the polymer in DMSO/glacial acetic acid mixture yielded curves that resembled the blank solution with no inflection, which could be an attributed to the insolubility of the polymer in glacial acetic acid. Therefore, these titrations were aborted and the amine titrations of the polymers were conducted in DMF. Titrations were not conducted in DMSO since titrations of the monomers in DMF suggest there would be no change in the titration results.

As expected, DMF influences the titration results observed in the titration of the polymers (figure 8). Both polymer titrations yield negative logarithmic curves with no inflection. They do show, however, an apparent change in the slope, which could be an indication of a change in the pH. Again, it is important to note the poor solvating power of DMF toward the polyamide in solution. In addition, these polymers could have a low concentration of amine end groups, which suggests the molecular weights of the polymers are greater than the size of oligomers (a molecule that has a few monomer units). However, the data for these titrations are inconclusive and cannot be accurately described because there is no confidence in the titration of the 1,6-hexamethylenediamine monomer previously discussed.

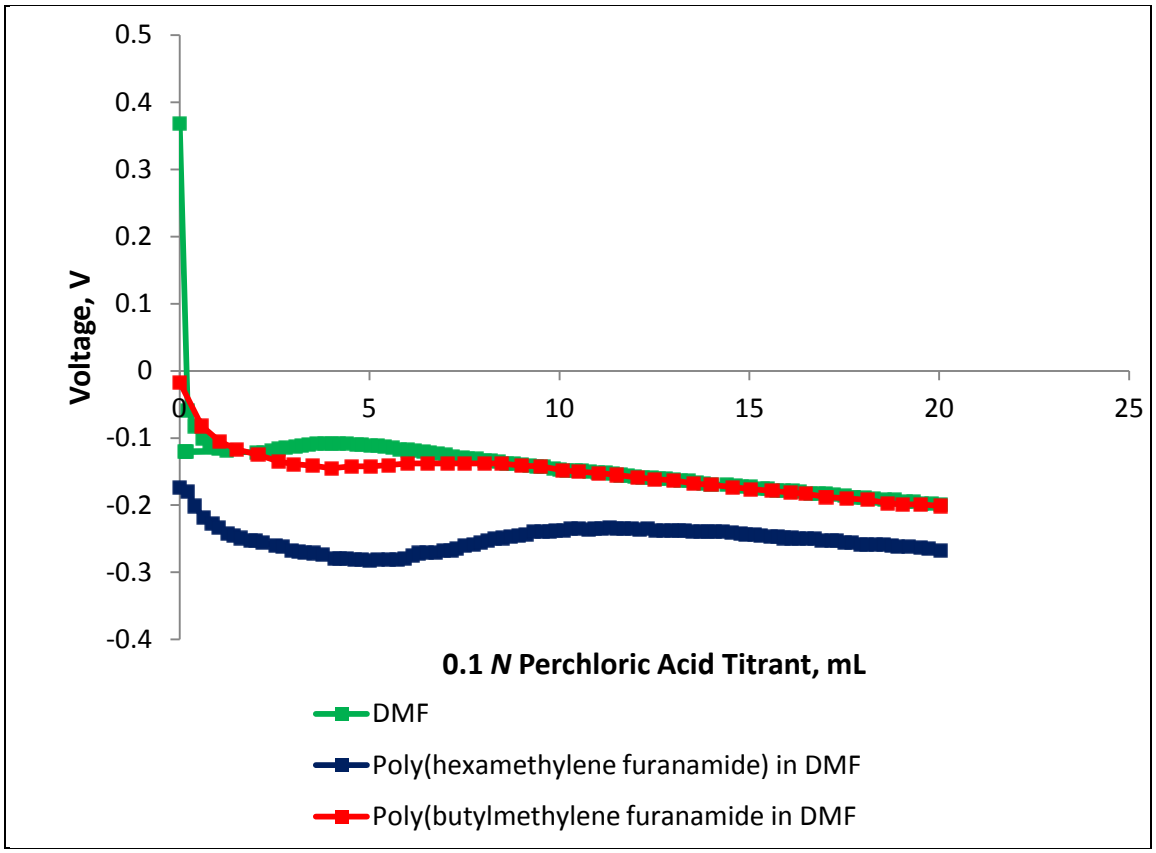

Figure 8. Amine titrations of biobased furan polyamides in DMF.

3.2 Acid Titration

The biobased furan polyamides are not soluble in isopropyl alcohol (table 1), which is the solvent of choice in ASTM D 664-11a for AN potentiometric titration. Therefore, a goal of this experimental work was to identify solvents that dissolve the polymer and allow for accurate molecular weight measurement through potentiometric titration.

The non-aqueous potentiometric titration of acid showed different results than the amine titrations. Titrations of the isopropyl alcohol blank and adipic acid are shown in figure 9. Isopropyl alcohol produced a titration curve with an increasing voltage from zero over the course of the titration and no inflection. There is no significant change in the pH of the blank, and the titrants are essentially equivalent throughout the titration. Adipic acid monomer in isopropyl alcohol was titrated in the acid titration. This plot was a sigmoidal curve that started at positive values but then descended to negative values with an end point at 10.5 mL. Based on this end point determined from the adipic acid titration in isopropyl alcohol, the EAN (31 mg/g) is significantly lower than the TAN (616.12 g/mol), and the $M_{n,\,COOH}$ (2990 g/mol) is significantly higher than the known molar mass.

Because the polymers were insoluble in isopropyl alcohol, adipic acid was titrated in DMF (figure 9), a solvent in which the polymers are soluble (table 1). By comparison, the titration curves were completely different from that of adipic acid in isopropyl alcohol and in DMF (figure 10) and produced EAN (1.19 mg/g) and $M_{n,\,COOH}$ (75,800 g/mol) that are again severely different from expected values. It is expected that titration in the different solvents would produce different titration curves as the dielectric constants and the solvent properties between DMF and isopropyl alcohol are different; however, there is no simple answer as to why titration in these solvents produce EAN and $M_{n,\,OH}$ values that are considerably incomparable.

Titrations of other monomers, succinic and 2,5-furandicarboxylic acids in DMF, produced similar titration curves: logarithmic with ill-defined inflections, as with the adipic acid in DMF (figure 9). At the beginning of the titration, the curve ascended for a short time before leveling off. An end point was determined by taking an average of the points in the inflection of the curve. Using the end point, the TAN, EAN, and the molecular weights of the monomers were determined by equations 5–7; the data is outlined in table 3. Thus, acid titration of adipic, succinic, and 2,5-furandicarboxylic acids in DMF proved to be unsuccessful in obtaining comparable results. The differences between the EANs were more than two orders of magnitude too low, and the $M_{n,\,OH}$ calculated for these monomers were orders of magnitude higher than the known molar mass.

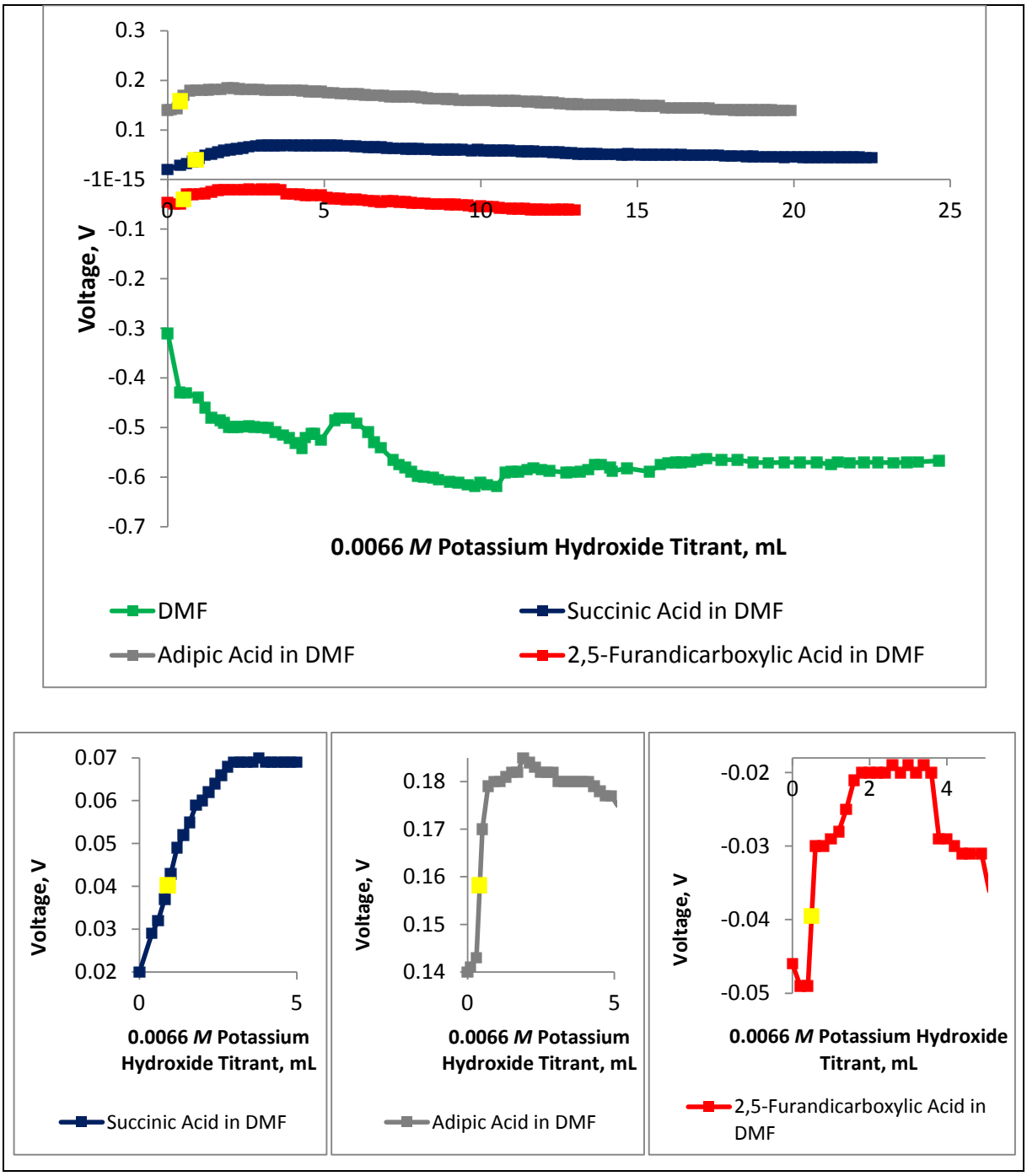

Figure 9. Acid titrations of monomers in DMF (graphs of single monomers below).

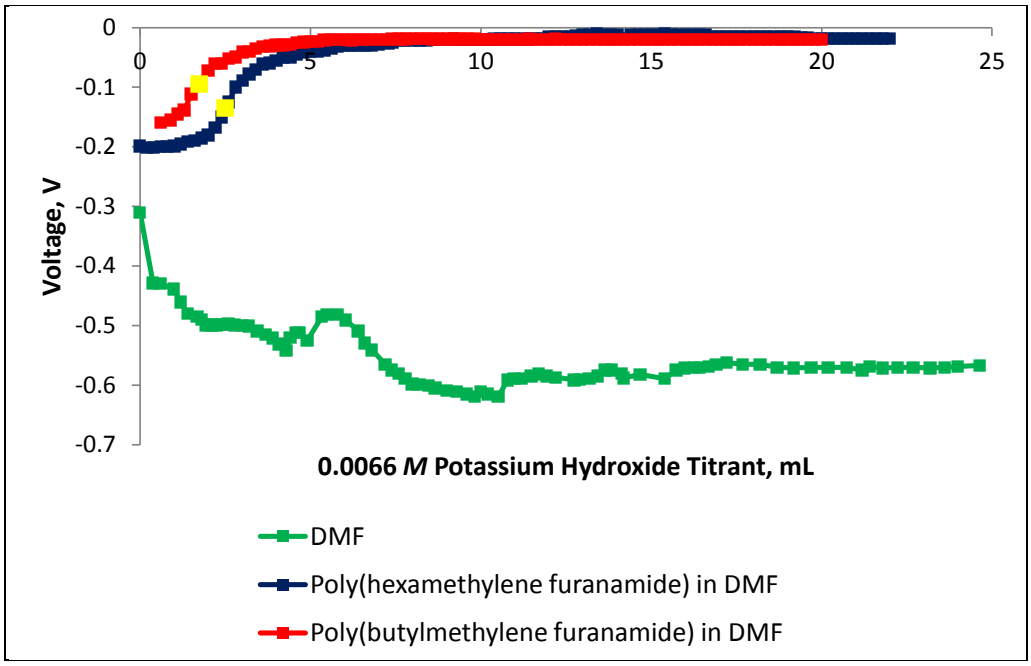

Figure 10. Acid titrations of biobased furan polyamides in DMF.

Table 3. Acid titration of adipic, succinic, and 2,5-furandicarboxylic acids in DMF.

Monomer	TAN (mg/g)	EAN (mg/g)	Molar Mass (g/mol)	$M_{n,\,COOH}$ (g/mol)
Adipic acid	616.12	1.19	146.14	75,800
Succinic acid	762.47	2.58	118.09	34,800
2,5-furandicarboxylic acid	576.85	1.48	156.09	60,700

The biobased furan polyamides produced similar titration curves to the monomers—logarithmic with inflections that occurred near the onset of the titration (figure 11). DMF as a base and carboxylic acids will likely interact, causing issues with the titration. This is likely not the effect because $M_{n,\,COOH}$ was lower than expected instead of higher. Thus, neat DMF may be a bad solvent for calculating AN since it can create solvation effects with solute. An average of the points in the inflection gave end points for both titration curves, which were used to calculate the AN and the experimental $M_{n,\,COOH}$. The $M_{n,\,OH}$ obtained using potentiometric titration was compared with the M_n determined by SEC and outlined in table 4. The $M_{n,\,COOH}$ value obtained by titration for poly(hexamethylene furanamide) does not compare to the value obtained by SEC, g/mol, and has a percent difference of 105. This difference could not be calculated for poly(butylmethylene furanamide) because attempts to determine M_n by SEC were unsuccessful due to low signal intensity. The SEC may be too high of an estimate because molecular weights are calibrated to those of polystyrene, which likely has a different chain stiffness than the biobased furan polyamides.

Table 4. Acid titration of the polymers in DMF.

Polymer	AN (mg/g)	$M_{n,\,COOH}$ (g/mol)	M_n (g/mol) by SEC	% Difference
Poly(hexamethylene furanamide)	5.02	12,000	39,000	105
Poly(butylmethylene furanamide)	0.0051	17,900	Undetermined; estimated M_w of 100,000	—

In addition to SEC data, attempts to quantify amine end groups via NMR were unsuccessful, as the NMR trace showed no visible intensity of amine end groups in the spectrum. This observation is consistent with the attempts to determine amine end group by titration.

According to Ibieta et al. (*14*), to accurately determine molecular weight of a polymer via potentiometric titration, $M_{n,\,titration}$, the molecular weight of all end groups present in the polymer must be calculated and incorporated into equation 8.

$$\frac{1}{M_{n,titration}} = \frac{1}{Mn,NH_2} + \frac{1}{Mn,COOH} + \frac{1}{Mn,\text{add'l end groups}} \,. \tag{9}$$

Because $M_{n,\,NH_2}$ of both polymers could not be obtained from potentiometric titration, a less accurate measure of $M_{n,\,titration}$ is determined. Thus, there is confidence with $M_{n,\,SEC}$ simply because the $M_{n,\,COOH}$ gives a value nearly half the amount of the $M_{n,\,SEC}$. This would also prove that non-aqueous potentiometric titration was useful in calculating M_n to a limited extent of confidence.

3.3 Discussion

Non-aqueous potentiometic titration can provide more accurate end group analysis than conventional methods that employ indicators, especially if a pH meter is used. According to the ASTM standards, the non-aqueous potentiometic titration setup included a voltmeter and a pH meter. There were a few variances to the setup and method employed in this work; for instance, the voltmeter used in the experiment was not digital and had little to no resistance to other the electromagnetic fields in the room (i.e., the air conditioner). The voltmeter did not have a pH meter attached; therefore, the pH was not monitored throughout the titration process. Amine titration of 1,6-hexamethylenediamine in various solvents proved that tracking pH would have provided a better understanding of the solvent effects encouraging the shift in the titration curve, particularly while using DMF as a solvent. Additionally, no Faraday cage was used in the experimental setup, so the titrations were conducted inside the chemical hood. The voltmeter was still sensitive to electromagnetic fields (i.e., the air conditioner) and other movements around the chemical hood, which caused the needle on the voltmeter to fluctuate, making it difficult to precisely read the measurements.

4. Conclusions

The ASTM standards used chlorobenzene (amine titration) and toluene, isopropyl alcohol, and chloroform (acid titration) as the solvent. Since the biobased furan polyamides were not soluble in these solvents, DMF was one of the few potential solvents. The limited solubility made it difficult to predict the results of the titration curve compared to the results in the ASTM standard. Also, DMF is not an ideal solvent for the titration procedure to produce accurate measurements of the monomers and the polyamides. Based on the amine titration curve produced from the 1,6-hexamethylenediamine monomer, if the polymers were soluble in glacial acetic acid, the $M_{n,\ NH2}$ of the polymers could have been determined, affording an accurate measure of the $M_{n,\ titration}$. Similarly, the solvent conditions used in the acid titrations did not allow for accurate measurements of both the monomers and polyamides, despite calculating a molecular weight value that was 105% different from the value calculated through SEC.

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