Mapping the Microstructure of Single-Site Ethylene/1-Hexene Copolymers Using Response Surface Methods

by

Venugopal Hegde

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in

Chemical Engineering

Department of Chemical and Materials Engineering
University of Alberta

Abstract

Polyolefins are a commercially important class of polymers made only of carbon and hydrogen atoms. Polyethylene accounts for a sizable fraction of commercial polyolefins, covering applications from packaging films, water tanks, biomedical equipment, bulletproof vests, and adhesives. The use of a wide variety of catalysts and multimodal molecular weight distribution (MWD) are some routes to modify the microstructure of polyethylene and its application properties. Polyolefins with multimodal MWD are commonly produced by polymerizing ethylene and 1-olefins in reactor cascades or using a single reactor with more than one catalyst type.

Designing polyethylene resins involves optimizing multiple microstructural distributions that result in targeted end-use properties. The end-use (secondary) properties are connected to the resin microstructure (primary property) by empirical equations called structure-property relationships. The goal of a polymer reaction engineer is to find polymerization conditions that achieve all or most of the properties in this wish list. The conventional solution to this problem is to develop fundamental polymerization kinetics models, estimate their parameters, and validate the model predictions vis-à-vis experimental data. However, the conventional route is a time consuming and expensive process. An alternative solution is to use response surface models, in which polymerizations are performed according to an optimal experimental design to develop statistically significant empirical models at a fraction of time and experimental effort required by phenomenological models.

In this thesis, response surface models were applied to quantify the microstructure of ethylene/1-hexene copolymers made with a single site metallocene catalyst in solution

polymerization. The molar weight averages and distributions, short chain branching (1-hexene content), and melting temperatures of these copolymers were modeled and predicted. The response surface models developed were subjected to acceptance criteria based on statistical significance tests. Explanatory validation on the effect of factors confirmed the validity of models. The forward process of predicting MWD for a given set of polymerization conditions was reversed to test the utility to reverse-engineer to find the reactor conditions for a defined resin microstructure.

Preface

The execution of the experimental design in Chapter 4 was done by Dr. Paul DesLauriers. GPC-IR measurements in the thesis work were performed by Dr. Saeid Mehdiabadi. All other aspects of the thesis are my original work.

Acknowledgments

I wish to express my sincere gratitude to many support pillars during my MSc program at the University of Alberta. First, I am grateful to my thesis supervisor Professor João B.P. Soares for believing in me to execute this project and allowing me to learn and grow. His guidance, motivation, and support have kept on track with project goals.

I want to thank my colleagues Raunil Raj and Amirreza Badri for supporting and teaching me throughout the project. Special thanks to Dr. Saeid Mehdiabadi for his insightful observations, discussions, and encouragement throughout my project. I would also like to acknowledge support, funding, and enlightening technical discussions with Dr. Paul DesLauriers and Dr. Jeff Fodor from the Chevron Phillips Chemical Company.

My deepest gratitude to my parents for their sacrifices, resoluteness, and affection inspired me to keep going. I would also like to thank my partner Nicole Anne Marie Rodriguez, for being a lifeline and standing by me through thick and thin. Finally, I would like to thank all the friends I met along the way in graduate school from whom I have learned a great deal.

Table of Contents

List of Figures

List of Tables

Nomenclature

Acronyms

ASTM	American Society for Testing and Materials
CAGR	Compounded annual growth rate
CAPE	Computer aided process engineering
CCD	Chemical composition distribution
CEF	Chain elution fractionation
COVID-19	Novel Coronavirus disease
DEAC	Diethyl aluminum chloride
DNA	Deoxyribonucleic acid
DoE	Design of Experiments
DoE	Design of experiments
ESS	Explained sum of squares
FBR	Fluidized bed reactor
GPC	Gel permeation chromatography
HDPE	High density Polyethylene
IR	Infrared
LDPE	Low density Polyethylene
LLDPE	Linear low-density Polyethylene
MAO	Methylaluminoxane
mHDPE	Metallocene HDPE
mLLDPE	Metallocene LLDPE
MMAO-12	Modified methylaluminoxane (MAO)
MSLF	Mean square lack of fit
MSPE	Mean square pure error
MTPA	Million tonnes per annum
MWD	Molecular weight distribution
NMR	Nuclear magnetic resonance
ODCB	Ortho dichlorobenzene
PE	Polyethylene
PP	Polypropylene
PVC	Polyvinyl chloride
RNA	Ribonucleic acid
RSM	Response surface methodology
RTD	Residence time distribution
SCB	Short chain branch
SCBD	Short chain branching distribution
SLD	Sequence length distribution
SLSQP	Sequential Least Squares Programming
SSE	Sum of squared error
SSF	Scale shift factor
TCB	Tricholorobenzene
TEA	Triethylaluminum
TIBA	Triisobutyl aluminium
TMA	Trmethylaluminum
TREF	Temperature rising elution fractionation
UA	University of Alberta
UHMWPE	Ultrahigh Molecular Weight Polyethylene
USD	United States Dollar
VLDPE	Very low-density Polyethylene

1. Introduction

1.1 Overview of Polymers, Polyethylene, and the Evolution of Polymer Research

COVID-19 disrupted humanity in the 21st century. Plastics emerged as our protector when the COVID-19 pandemic hit the world. Plastics form a large proportion of medical equipment, personal protective equipment (PPE), and consumer goods packaging. The word "plastic" means "pliable and easily shaped".[1] Today the broad term plastic refers to polymers.[1] The first human-synthesized polymer, celluloid, was invented in response to an ivory shortage in 1863.[2] Polymers were vital in World War II: perspex in plane cockpits, plexiglass for plane windows, polyethylene in radars, and nylon in parachute cords, helmets, and liners.[1,3] Polymers substitute metals, wood, paper, and many other conventional materials. Natural and synthetic polymers have enhanced the quality of human life for a very long time.

Polymers are defined simply as materials containing many repeat units. This arises from "poly", meaning many, and "mer", meaning units. Polymers can be classified into two broad classes: synthetic and natural.[4] Molecules that store and express genetic information, DNA and RNA, are natural polymers.[5] Proteins (such as keratin in hair and nails), cellulose, and natural rubber are also natural polymers.[4,6] Synthetic polymers are human made and are often petroleum derivatives. Polyethylene (PE), polypropylene (PP), nylon, polyvinyl chloride (PVC) and epoxies are examples of some common synthetic polymers.[7]

Polymers can be categorized according to their physical responses to heat as thermoplastics or thermosets. Thermoplastics soften and melt on heating. They form products in heat-softened (thermoforming) or in liquid state (such as extrusion or injection molding) processes.[8] Polyethylene, polypropylene, and polyvinyl chloride are thermoplastics. Thermosets cannot be reused by heating and are often formed by an initial curing process that sets their properties.[9] Bakelite, polyurethane and silicone resins are thermosets.[10]

Polyolefins are a class of synthetic polymers formed when olefins (hydrocarbons with a C=C double bond) polymerize to form macromolecules. Polyethylene and polypropylene are the most important polyolefins. Polyolefins are the biggest class of thermoplastics. Their market value is slated at USD 300 billion, with a compounded annual growth rate (CAGR) of 7-8 %.[11,12] Polyethylene is expected to be the largest segment, with a market share of 30 % by 2022.[11] The global production of polyolefins is forecasted to surpass 180 MTPA.[11] Polyethylene is the polyolefin with the shortest repeat unit $(-CH_2-CH_2-)_n$, formed when ethylene polymerizes. Usually, α-olefins are copolymerized with ethylene to form polyethylene with short chain branches (SCB). The average content and distribution of SCBs, long chain branches, types of α-olefins, and the molar weight distribution allow for a plethora of different microstructures for polyethylene.

Polyethylene is classified by degree of crystallinity as high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), low density polyethylene (LDPE), and very low-density polyethylene (VLDPE), as shown in Figure 1-1. Polyethylene is a semi-crystalline polymer that combines crystalline and amorphous phases, each phase assumed to have uniform densities.[13] The classification of polyethylene by density has a historic reason: density is easier and quicker to measure than more elaborate polymer microstructure distributions. Moreover, it is easier to compare singular values, such as density or melt flow index (MFI), than microstructural distributions. Density, however, is not a fundamental polymer property, but a secondary property that depends on the polymer microstructure and processing conditions.[14] However, density may be treated as a fundamental property by controlling processing conditions though standardized measurements such as ASTM D4703, ASTM D4883, and ASTM D1505.[14] The density ranges are 0.94-0.97 g/cm^3 for HDPE, 0.90-0.94 g/ cm^3 for LDPE and LLDPE, and 0.86-0.90 g/ cm^3 for VLDPE.

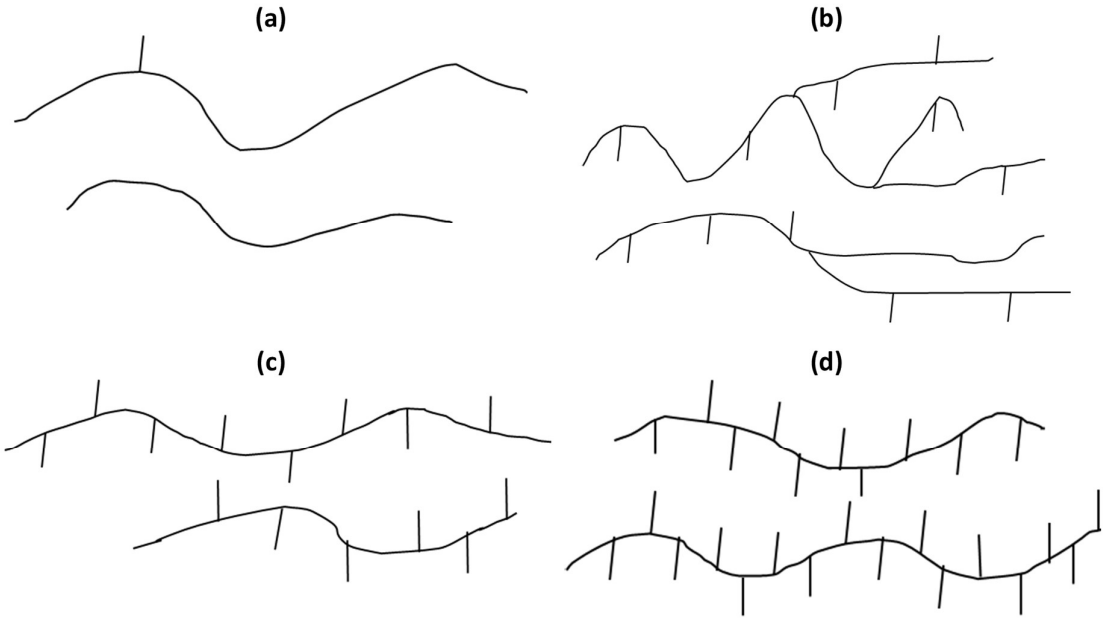


Figure 1-1 Classification of polyethylene based on density: a) HDPE, b) LDPE, c) LLDPE, d) VLDPE.

These classes have different morphologies that result in different crystallinities. HDPE (Figure 1-1.a) has linear chains with no, or very few, SCBs. Hence, these chains form large crystallites with smaller amorphous domains in the solid state, resulting in higher overall densities. The morphology of LDPE (Figure 1-1.b) is a consequence of the free radical polymerization used to make it in high-pressure processes. LDPE contains both short and long chain branches, which lower its crystallinity and, therefore, density. LLDPE (Figure 1-1.c) is linear like HDPE but has densities closer to LDPE because of the presence of SCBs distributed randomly on their linear carbon backbone. The average separation between SCBs is 25-100 backbone carbon atoms.[13] VLDPE (Figure 1-1.d) has a higher frequency of SCBs, separated by 7-25 backbone carbon atoms.[13] The abundance of SCBs results in a mostly non crystalline polymer. One other important class of polyethylene is ultrahigh molecular weight polyethylene (UHMWPE). UHMWPE has high molecular weight averages (of several million Da) with the morphology of HDPE.

The near infinite combinations of microstructural distributions possible for polyethylene make it a versatile material. To access these combinations, one requires quantitative understanding of the relationships between input production parameters (monomer concentrations, reactor

temperature, reactor residence time) and product microstructure. These relationships can be subdivided into three scales:[15] 1) Microscale/kinetic modeling, 2) Mesoscale/thermodynamic modeling, 3) Macroscale/reactor modeling.

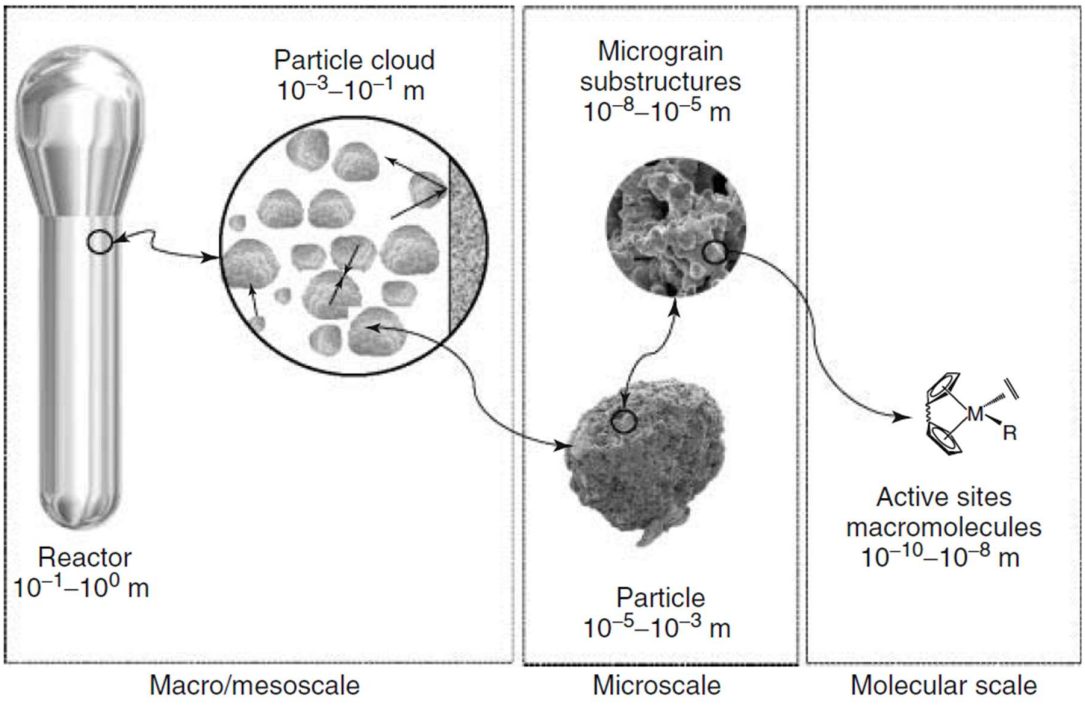


Figure 1-2 Length scales in a commercial reactor.[16]

Figure 1-2 shows a fluidized bed reactor (FBR) used to produce polyethylene or polypropylene on large scale. Microscale models quantify all the elementary reactions at the active sites of the catalyst and predict the chain microstructure using the conditions at the active sites. Mesoscale models quantify the thermodynamic equilibrium between phases (in the case of FBR, the growing polymer and the gas phase), heat and mass transfer within the phase (the concentration and temperature gradients within the growing polymer particles).[15] Mesoscale models generate the reaction conditions profile which informs microscale models. Macroscale models quantify macro-mixing in the reactor (through inputs like residence time distribution, RTD), reactor dynamics, process control, and overall energy and mass balances.[15]

These three modelling scales are interconnected and gather all phenomena taking place in the reactor. These multiscale models require the solution of a system of algebraic-differential equations that can become rather involved. Since all mathematical models are only simplified

descriptions of reality, the choice of a model involves a trade-off between usefulness and level of details.

Microscale/kinetic models are related to the product microstructure and the macroscale operation of the reactor. The kinetic rate constants tie in both aspects of interest: polymer microstructure and reaction rates. Hence, accurate measurements of kinetic parameters are essential to build an usable reactor model. Complete kinetic models require the data of many polymerization experiments under controlled process conditions. The values reported in the literature for the kinetic rate constants may only be used as approximations, because they depend on the catalyst/cocatalyst system, poison levels, and on the polymerization mechanism employed to estimate them.[17] Microstructure analysis methods, such as GPC (gel permeation chromatography), CEF (crystallization elution fractionation), TREF (temperature rising elution fractionation), and NMR (nuclear magnetic resonance) provide additional data from which some kinetic parameters or a group of lumped parameters may be estimated. However, these microstructure analysis methods introduce a degree of uncertainty and can only be a part of the solution for the large scheme kinetic parameter estimation. These approaches are a good starting point for further fine tuning and data reconciliation with observed behavior.[15] Therefore, for global process models to predict the behavior of commercial reactors, parameter finetuning and experimental support are required.[17]

It is instructive to retrace history of the stages of development of polymer science and engineering to put the state of the art in context. Scott and Penlidis[18] described the chronological progress shown in Figure 1-3. The inception of the first synthetic polymers came about in the late 1800s-1940s with the vulcanization of rubber, invention of bakelite, nylon, viscose silk, and thiourea formaldehyde.[19] The focus in this period was the synthesis of polymers based on organic and physical chemistry principles.[18] The 1940s-1960s saw rapid industrialization, partly attributed to the second world war and its aftermath. Progress in technology, reaction engineering and chemistry led large scale production of polymer commodities.[18] The invention of catalysts by Ziegler and Natta to make stereospecific polypropylene and polyethylene in 1950s proved to be a watershed moment in the development of polyolefins. This was important as it allowed the low-pressure production of polyethylene.

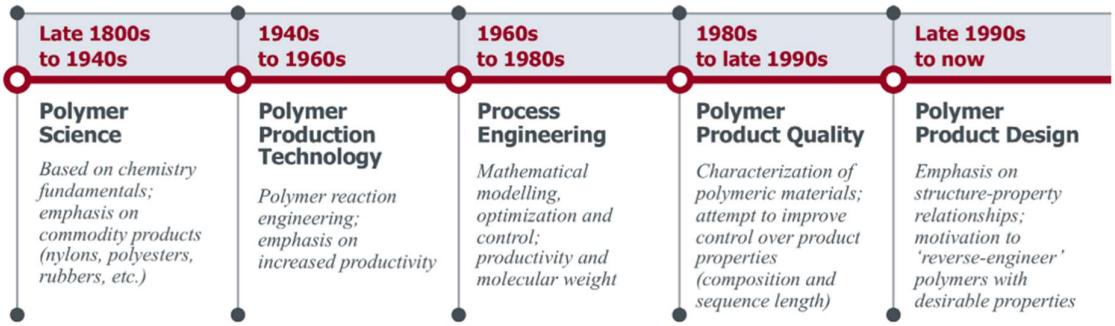


Figure 1-3 Progress of polymer science and engineering.[18]

The central theme in the 1960s-1980s was process engineering. A gamut of reactor operation combinations such as batch, continuous, semi-continuous, isothermal, and temperature-profiled reactors were established on a commercial scale.[18] Tools such as optimization, modeling, and process control led the era of large scale production with emphasis on optimality.[18] The boom in use of mathematical tools in polymers coincided with "computer aided design" or "computer aided process engineering (CAPE)".[20] The serendipitous discovery of methylaluminoxane (MAO) as an activator for metallocene precursors stimulated an appetite for academic and industrial metallocene research.[21] The period from the 1980s to the late 1990s saw an evolution of emphasis on polymer product quality, the so called "quality revolution".[18] The quality revolution unfolded in synergy with the advances in statistical process control[22] and computational capacity.[18,23] Increased capabilities in data logging, sensors and multivariate analyses techniques allowed the quest of reverse engineering the process. Scott and Penlidis[18] described the reverse process as predicting polymerization conditions and recipes that would make polymers with the desired microstructures.

Optimal polymer design is a pursuit of the best choice of catalyst and reactor conditions that minimize the cost of production with robust reactor operability. In the context of most metallocene LLDPE (mLLDPE) and HDPE (mHDPE) resins, this translates into selecting the type metallocene catalyst and co-catalyst, the catalyst support, and the polymerization conditions. This design process is often limited by reactor operating limits (such as pressure and temperature), downstream resin processing capacity, and reliable and robust supply of the catalyst system.

1.2 Motivation and Objectives

Polyethylene resin design is a multi-objective optimization problem with many opposing targets. The conventional approach involves developing fundamental kinetic models to study several aspects of the polymerization process, such as catalyst deactivation, propagation, and chain transfer. However, the experimental effort involved in this process is not justified in some cases, such as catalyst screening for a specific target resin. In such cases, it may be better to have a tool that can describe essential features of the catalyst response within a specific range of polymerization conditions. The focus of this thesis is to develop a response surface methodology as a tool that can aid and accelerate such evaluations. The tool that I developed models many features of the resin microstructure. Once a forward prediction tool was developed, it was then used to target resins of defined microstructure by determining optimal polymerization conditions (reverse model).

1.3 Thesis Outline

This thesis is divided into five chapters. Chapter 1 provides an overview of polyethylene, evolution of polymer process modeling, and the motivation for this thesis. Chapter 2 describes the state of the art in polyethylene microstructural characterization, catalysts for ethylene polymerization, integrated variance optimal designs, response surface models, and principles of stepwise selection. Chapter 3 describes the materials, polymerization procedures, and characterization techniques used in this research. Chapter 4 discusses the experimental results, response surface modeling for molecular weight averages, short chain branching, melting temperatures, an extension of the modeling approach proposed by DesLauriers et al.[24] to model the MWD, augmentation of the MWD modeling by deconvolution, explanatory validation, and the reverse process to design targeted resins. Finally, Chapter 6 summarizes the most important results of this thesis and makes recommendations for future work.

2. Literature Review

2.1 Polyethylene Microstructural Distributions and Characterization

The main microstructural distributions for polyethylene are the molecular weight distribution (MWD), the chemical composition distribution (CCD), and the long-chain branch distribution (LCB). The MWD is the most fundamental primary property of a polyolefins (and of polymers in general) because it strongly influences their mechanical and melt flow properties. The CCD influences the crystallization behavior, and the LCB affects melt strength and rheology. A short description of the analytical techniques used in this thesis project are given in the following sections.

2.1.1 Molecular Weight Distribution

The molecular weight distribution (MWD) is the most important primary property of polyethylene. The molecular weight of polyethylene varies from oligomeric resins, with molecular weights in the range of few hundreds (such as hot melt adhesives) to ultra-high molecular wight polyethylene (UHMWPE), which is used in high-abrasion wear parts, liners, and walkways. Due to the statistical nature of the coordination polymerization mechanism used to make polyethylene, the polymer consists of a blend of chains with vastly different molecular weights. The resulting MWD is usually characterized by its averages, M_w, M_n, M_z, and M_{z+1}.

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \tag{2.1}$$

$$M_w = \frac{\sum N_i {M_i}^2}{\sum N_i M_i} = \sum w_i M_i \tag{2.2}$$

$$M_z = \frac{\sum N_i {M_i}^3}{\sum N_i {M_i}^2} \tag{2.3}$$

$$M_{z+1} = \frac{\sum N_i {M_i}^4}{\sum N_i {M_i}^3} \tag{2.4}$$

where, M_i is the molecular weight of the polymer chains, N_i is the number of the polymer chains with molecular weight M_i, and w_i is the mass fraction of the chains whose molecular weight is M_i.The breadth of the MWD is represented by the ratio of M_w to M_n, called dispersity. Sometimes, M_w to M_n (and higher averages) are not enough to unequivocally represent the MWD. For instance, two polymer samples could have similar molecular weight averages and vastly different MWDs.

Expressions for M_w, M_n, M_z, and M_{z+1}can also be defined for continuous distributions,

$$M_n = \frac{1}{\int \frac{w\,(\log M)}{M}\,\mathrm{d}(\log M)} \tag{2.5}$$

$$M_w = \int M\, w(\log M)\,\mathrm{d}(\log M) \tag{2.6}$$

$$M_z = \frac{\int M^2\, w(\log M)\,\mathrm{d}(\log M)}{\int M\, w(\log M)\,\mathrm{d}(\log M)} \tag{2.7}$$

$$M_{z+1} = \frac{\int M^3\, w(\log M)\,\mathrm{d}(\log M)}{\int M^2\, w(\log M)\,\mathrm{d}(\log M)} \tag{2.8}$$

High-temperature size exclusion chromatography (SEC), also known as high-temperature gel permeation chromatography (GPC), is the most common technique to measure the MWD of polyethylene (schematic shown in Figure 2-1). Most commercial polyethylene resins are soluble above 120 °C in solvents such as trichlorobenzene (TCB) or orthodichlorobenzene (ODCB).[16]

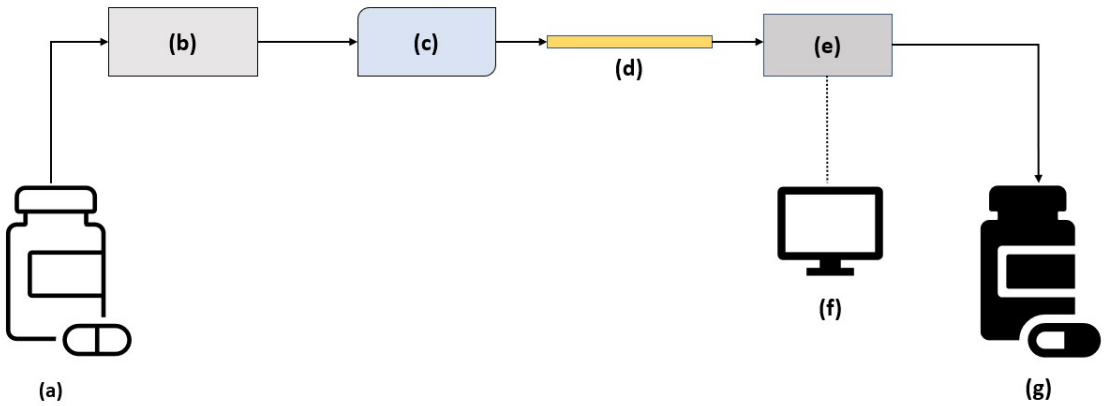


Figure 2-1 Schematic of a size exclusion chromatographer: a) solvent reservoir, b) pump, c) injector, d) series of columns, e) detector, f) data recording computer, g) waste tank.

As its name suggests, SEC fractionates polymer chains based on their hydrodynamic volumes in solution. The hydrodynamic volume of a polymer chain depends on its degree of polymerization, branching type and frequency, type of solvent, temperature, and polymer solution concentration. To eliminate the effect of polymer solution concentration, the analysis is performed at the lowest possible concentration.

SEC uses a series of columns packed with cross linked gels (thus the name gel permeation chromatography) having pores of different diameters. The polymer solution is introduced into the mobile phase as a pulse injection. The time spent by a polymer chain to exit the column set (elution time) depends on its hydrodynamic volume. Polymer chains with higher hydrodynamic volumes penetrate in fewer pores and leave the column earlier, whereas smaller polymer chains enter more pores and elute later. A mass detector calculates the polymer concentration exiting the column set. Calibration curves relate polymer molecular weight to elution volume (or retention time). A generalized procedure to convert a SEC elution curve to MWD is shown in Figure 2-2.

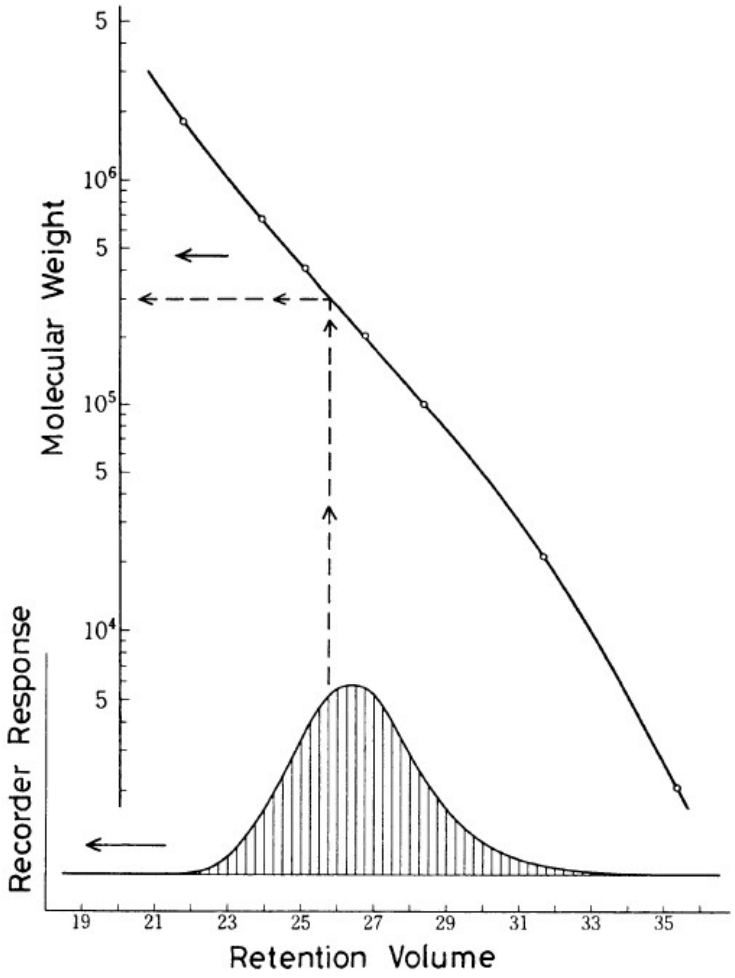


Figure 2-2 Converting elution curves to MWD.[25]

2.1.2 Short Chain Branching

When ethylene is copolymerized with comonomers such as 1-butene, 1-hexene, or 1-octene, the formed SCBs decrease the crystallinity and density of the copolymer. SCBs have a great influence on the mechanical properties of polyolefins. The placement of the SCBs along the MWD also affects the performance of these resins. For instance, polyethylenes with more SCBs on the longer chains have better environment stress crack resistance.[26] SCB can be measured along the MWD (Figure 2-3) when an IR or Fourier-transform infrared (FTIR) detector is connected to the exit of the GPC column. In these methods, polymer fractions with different elution times/molecular weights separated by the GPC columns pass through a heated cell where they are exposed to IR radiation.[16]

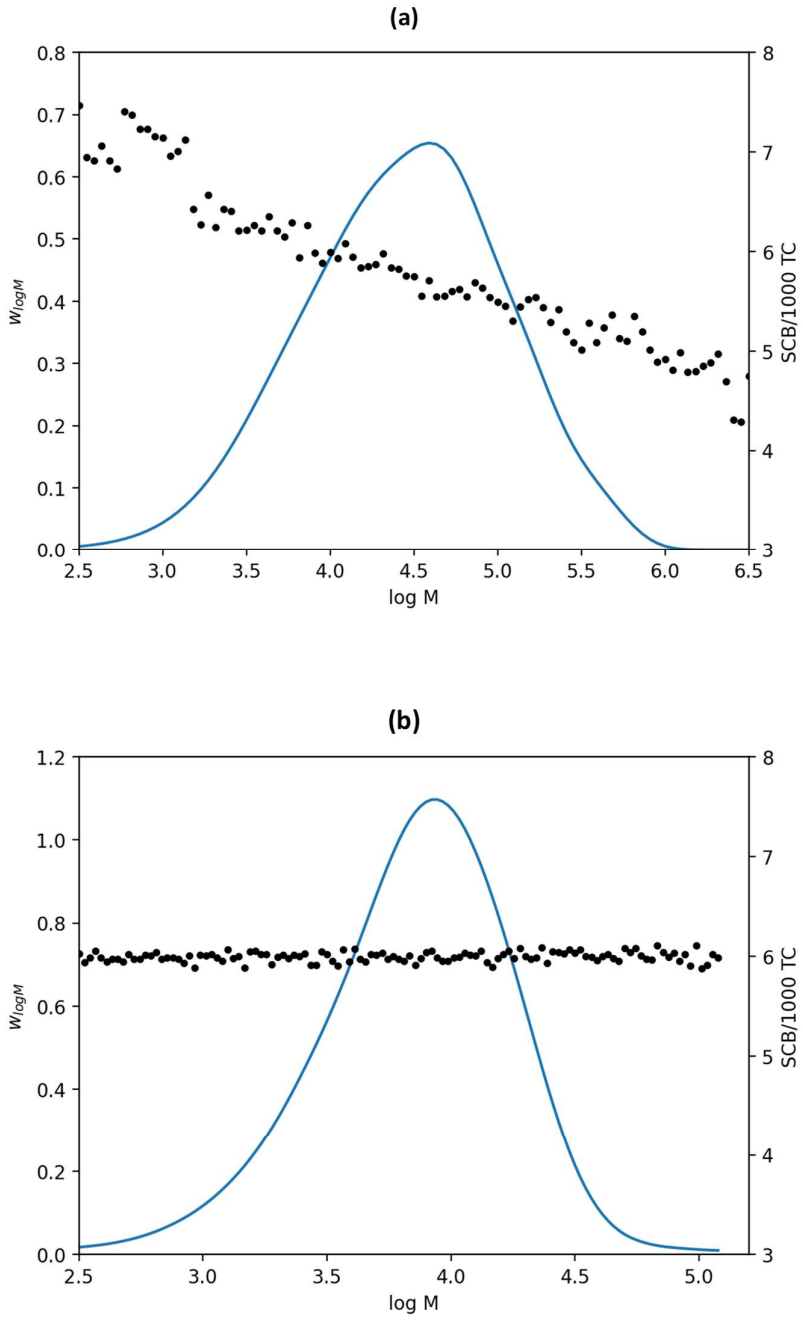


Figure 2-3 SCB across the MWD: a) typical Ziegler Natta polyethylene, b) metallocene polyethylene.

2.1.3 Differential Scanning Calorimetry

Differential scanning calorimetry is a technique that measures thermal transitions such as melting, crystallization, and glass transition. The DSC measurement chamber is equipped with two pans. The polymer sample is placed in the sample pan, while the reference pan remains empty. Both pans are subjected to a temperature profile predetermined by the user. As the pans are heated, their temperatures begin to rise. The differential heat absorbed by the sample pan is recorded as a function of temperature. The resulting plot of the differential heat is recorded against temperature. The crystallization temperature (T_c) is the temperature at which an isotropic liquid crystallizes into a solid when cooled. In Figure 2-4, as the liquid polymer sample is cooled from 160 ºC, it crystallizes and releases heat.

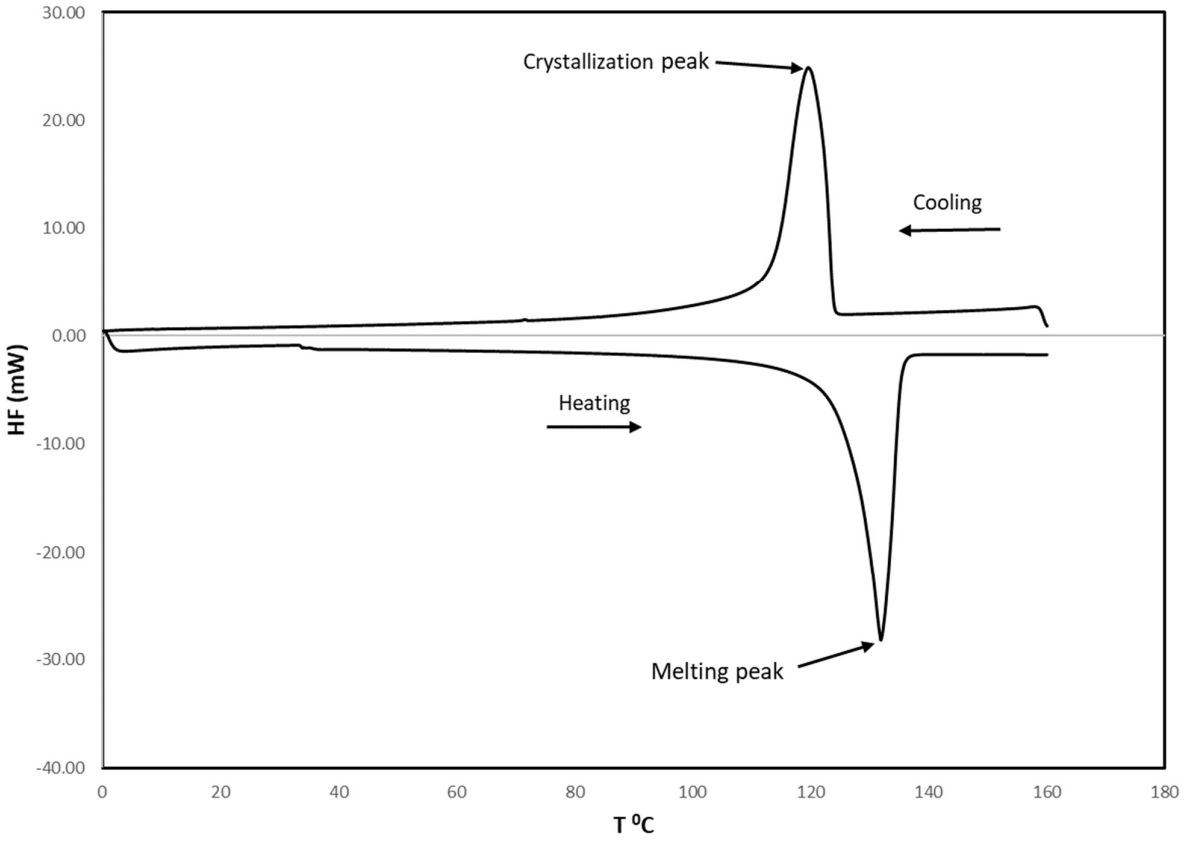


Figure 2-4 DSC thermogram of a polyethylene sample: cooling and heating sections.

When the same sample is heated from the solid state, it melts at a higher temperature than it crystallized, as also shown in the endothermic melting peak (T_m) in Figure 2-4. For ethylene/α-olefin copolymers, the melting temperature is corelated with the fraction of comonomer in the

sample. The higher the comonomer content, the smaller the crystals and the lower the melting temperature.

2.2 Catalysts for Ethylene Polymerization

The catalyst is the key factor when synthesizing ethylene/α-olefin copolymers because it defines the microstructural characteristics of polyethylene. This section provides a brief overview of the different types of catalysts for olefin polymerization.

In 1953, the German chemist Karl Ziegler discovered a catalytic system able to polymerize ethylene into high molecular weight linear polyethylene, which could not be made by free radical polymerization.[27] The system contained of $TiCl_4$ and Al $(Et)_3$, as shown in Figure 2-5.

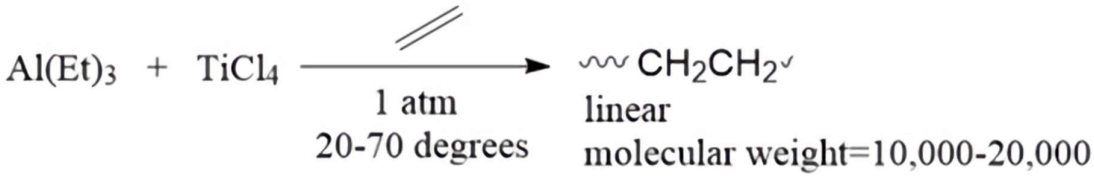


Figure 2-5 High molecular weight polyethylene synthesized by Ziegler's catalytic system.[27]

The Italian chemist Giulio Natta discovered that the polymerization of propylene with a similar catalyst produced stereoregular polypropylene, either syndiotactic or isotactic (Figure 2-6). Considering these important discoveries, Karl Ziegler and Giulio Natta shared the Nobel Prize in Chemistry in 1963.[27]

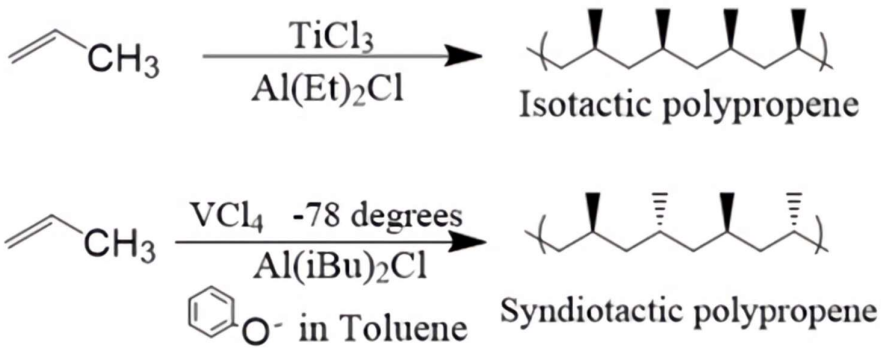


Figure 2-6 Giulio Natta's catalyst system.[27]

Ziegler–Natta catalysts are formed by a transition metal salt of metals from groups IV to VIII (catalyst precursor) and a metal alkyl of a base metal from groups I to III (cocatalyst).[16] The cocatalyst activates the catalyst precursor in a two-step process of alkylation and reduction of the transition metal centers. Commonly used cocatalysts include alkyl aluminum compounds such as triethyl aluminum (TEA), trimethyl aluminum (TMA), and diethyl aluminum chloride (DEAC). A typical heterogeneous Ziegler–Natta catalyst consists of $TiCl_4$ supported on SiO_2 or $MgCl_2$. $TiCl_4$ and $MgCl_2$ form a mixed crystal in which the $TiCl_4$ active sites are easily accessible to the ethylene.[16]

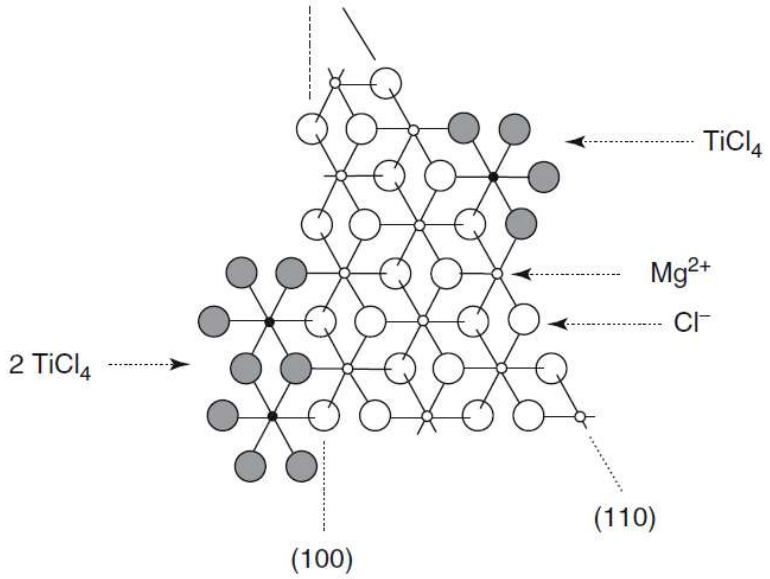


Figure 2-7 Structure of a generic Ziegler–Natta catalyst.[16]

Ziegler–Natta catalysts make polyolefins with non-uniform microstructures, with broad and sometimes multimodal MWDs and CCDs. The nonuniform microstructure of the polyolefins produced with Ziegler-Natta catalysts is attributed to the presence of the multiple site types on these catalysts. Most commercial LLDPE resins are made with heterogeneous Ziegler-Natta catalysts.

Each site type can be characterized by a unique set of polymerization kinetic constants. Therefore, each site may be assumed to behave like a single site catalyst, producing polyolefins with narrower MWD and CCD.[28] This framework forms the basis for the development of mathematical modeling approaches such as MWD and CCD deconvolution for polymers made with Ziegler-Natta catalysts.[28]

Natta and Breslow used metallocene catalysts in 1957 to polymerize olefins using aluminum alkyl compounds such as TMA and TEA.[16] They noted that the polymerization rates were low because of bimolecular deactivation reactions. The serendipitous discovery that methylaluminoxane (MAO) activated and stabilized metallocene catalysts led to a revolution in the polyolefin manufacturing industry. Metallocene polyolefins offer superior mechanical properties due to their narrow MWD, but they are also harder to process than similar Ziegler-Natta counterparts due the absence of low molecular weight lubricating chains. The introduction of long chain branches (LCB), however, even at low levels, aids greatly in processability. Metallocene catalysts are often called sandwich compounds. They consist of transition metal centers sandwiched between two cyclopentadienyl rings, or ring derivatives, as shown in Figure 2-8.

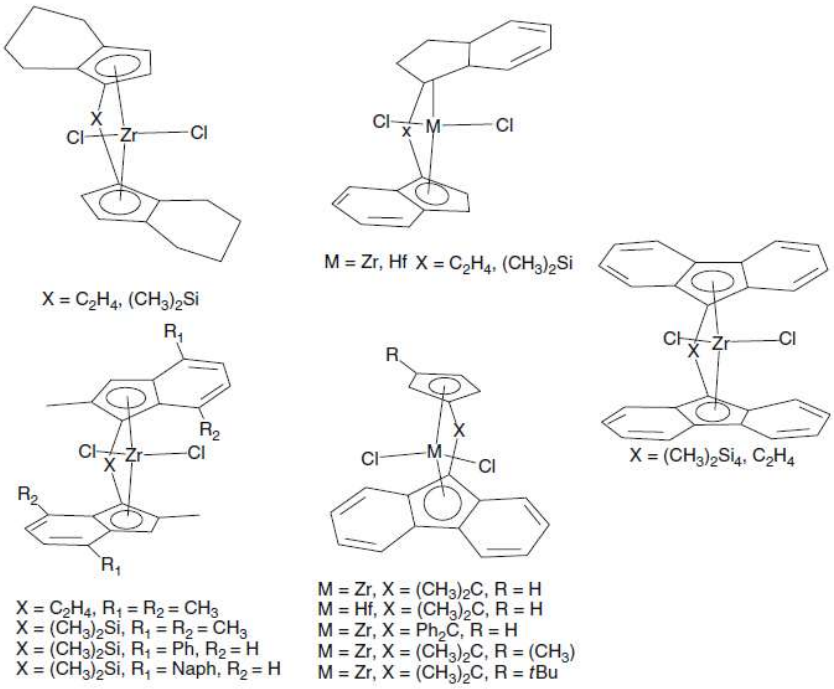


Figure 2-8 Some common metallocene catalysts.[16]

2.3 Integrated Variance Optimal Design

The main objective of this thesis is to predict the microstructure of polyethylenes made with metallocene catalysts using empirical models. For these models to work, one must ensure the training data is collected at design points that decrease the number of experiments and maximize the prediction ability of the model.

We used the Stat Ease software to generate the three-factor optimal design shown later in Table 4-2. Optimal design methods aim at minimizing a given statistical criterion. We used a class called integrated variance design, which minimizes the average prediction variance. A comparison of a few optimal designs and statistical criteria is shown in Table 2-1.

Table 2-1 Different types of optimal designs.[29]

Optimal design	Statistical criterion minimized
A-optimal	Average parameter variance
D-optimal (determinant optimal)	Generalized parameter variance
E-optimal (extreme optimal)	Largest eigenvalue (worst-estimated direction)

L-optimal	Linear combination on components of the variance matrix
G-optimal	Global worst standardized predictive variance
V-optimal or IV-optimal variance optimal or integrated variance optimal	Average predictive variance over a region of interest

The IV optimal design minimizes the variance of predictions over the experimental space. The design can be further customized by weighing the prediction variance with respect to probability distribution of points in the experimental space.[30] The ordered list of factors contained in the design of experiments (DoE) (values for each input variable) is written in matrix form and called the design matrix. The criterion to minimize the prediction variance is applied to the design matrix. These designs are executed by randomly generating a set of design points, substituting values in the design matrix to minimize the average prediction variance successively by co-ordinate exchange algorithms until no improvements can be made.[31] Co-ordinate exchange algorithms generate locally optimal design. Therefore, these designs are run many times to look for the global optimum within the experimental space.

We chose this design for our study because we were interested in minimizing the prediction variance of the MWD. As will be discussed later, the $\log M$ space in the MWD was discretized into 100 slices to be modeled using RSM models. Hence, response from 100 models at discrete $\log M$ points were used to generate models to predict the MWD of polyethylene under different conditions.

2.4 Response Surface Methods

Experiments aimed at describing responses as functions of input factors are known as response surface methods (RSM). Response surface modeling also allows one to find input values that maximize or minimize the responses. Polynomials are the simplest functions that can be used with response surface methods.

The choice of the order of the polynomial model depends on: a) the intended use of the RSM; for screening/sensitivity analysis models, lower order polynomials might suffice, whereas for optimization models, higher order polynomials might be necessary, b) the experimental resources available; higher order polynomials cannot be used if only a few experiments can be

performed, and c) the prior knowledge of the model structure; in some cases one might be interested in using terms in models that incorporate an element of interpretability based on prior knowledge about the system.

Model accuracy depends on the number of design points versus the number of parameters that must be estimated, the shape of the true response function, and the span of the experimental space. For most small experimental design spaces, a smooth response can be modeled with a second order polynomial.[32] When trying to find the structure of a surface response model, it is instructive to keep in mind the famous aphorism by the statistician George Box: "All models are wrong, but some are useful."

A second order polynomial was used to model the MWD of our polyethylene samples,

$$w(log\ M) = a_1T^2 + a_2E^2 + a_3R^2 + b_1T\,E + b_2T\,R + b_3E\,R + c_1T + c_2E + c_3R + d_1 \quad (2.9)$$

2.5 Stepwise Selection

Stepwise regression is an automatic procedure that selects the terms (predictor) to be included in the regression model. The model in Equation (2.9) comprises a maximum of ten terms. The stepwise selection builds the model from this set of terms by adding and deleting them in the model.[33]

The steps involved in a stepwise regression for a response y that depends on the predictor variables $x_1,\ x_2,\ x_3, \ldots\ x_p$ are: [33]

1. Choose a significance level, α_E, to decide when to add a predictor variable in the model.
2. Choose a significance level, α_R, to decide when to delete a predictor variable from the model.
3. Fit each of the single predictor models — $y = f_1(x_1),\ y = f_2(x_2), \ldots,\ y = f_p(x_p)$ to the experimental data.
4. Select the predictor with the smallest p-value (for the t-test) among all single predictor models. For instance, select x_1 if it has the smallest p-value (for the t-test) which must be also lower than α_E.

5. Fit all two-predictor models that include x_1 (supposing it was selected in step 4) — $y = f_{12}(x_1, x_2),\ y = f_{13}(x_1, x_3), \ldots,\ y = f_{1p}(x_1, x_p)$ to the experimental data.
6. Among all the two-predictor models, select the next predictor with the smallest p-value (for the t-test) among all the two-predictor models. Let's suppose x_3 was selected from the model $y = f_{13}(x_1, x_3)$. Check if the p-value of x_1 in the model $y = f_{13}(x_1, x_3)$ is less than α_R. If the p-value of x_1 (for the t-test) is greater than α_R, remove x_1 from the list of selected predictors, else retain it.
7. Repeat this process until no more terms can be added to the list of selected predictors.

At each step in the process when a predictor is added (forward step), the p-value of all the selected predictors is tested. If any one or more of the predictors have a p-value greater than α_R, they are removed from the list of selected predictors (backward step). The result of stepwise selection is that we end up with statistically significant predictors. In our case, $\alpha_E = 0.01$ and $\alpha_R = 0.05$ was used. The stepwise selection process was used to select the predictors for all the models built in this project. The stepwise selection is illustrated through an example (for the data shown in Table 2-2). A, B, and C are the independent variables and Y is the dependent variable. Set $\alpha_E = 0.01$ and $\alpha_R = 0.05$.

Table 2-2 Data for illustration of stepwise selection.

A	B	C	Y
73	80	30	152
93	88	32	185
89	91	30	180
96	98	41	196
73	66	50	142
53	46	50	101
69	74	70	149
47	56	30	115
87	79	40	175
79	70	41	164
69	70	65	141
70	65	60	141
93	95	55	184
79	80	45	152
70	73	55	148
93	89	55	192
78	75	20	147
81	90	21	183

88	92	25	177
78	83	45	159
82	86	40	177
86	82	41	175
78	83	85	175
76	83	58	149
96	93	85	192

Fit single predictor models ($Y = f_A(A),\ Y = f_B(B)$, $Y = f_C(C)$) shown in (Table 2-3 to Table 2-5). The p-value for the factor A (5.29 x 10^{-33} shown in Table 2-3) is the lowest and is also lower than $\alpha_E = 0.01$. Hence A is selected at this step.

Table 2-3 Single predictor model with factor A.

Y	**Coef.**	**St. Error**	**t**	**p-value**	**95 % CI**
A	2.05	0.02	100.33	5.29 x 10^{-33}	(2.00,2.09)

Table 2-4 Single predictor model with factor B.

Y	**Coef.**	**St. Error**	**t**	**p-value**	**95 % CI**
B	2.04	0.02	86.98	1.61 x 10^{-31}	(1.98,2.08)

Table 2-5 Single predictor model with factor C.

Y	**Coef.**	**St. Error**	**t**	**p-value**	**95 % CI**
C	3.05	0.25	12.24	8.29 x 10^{-12}	(2.54,3.56)

The two factor models ($Y = f_{AB}(A,B),\ y = f_{AC}(A,C)$) are fit and the results are shown in (Table 2-6 and Table 2-7). The p-value for the factor B (2.9 x 10^{-3} shown in Table 2-6) is the lowest and is also lower than $\alpha_E = 0.01$. Hence B is selected at this step.

Table 2-6 Two predictor model with factors A and B.

Y	**Coef.**	**St. Error**	**t**	**p-value**	**95 % CI**
A	1.20	0.26	4.72	9.4×10^{-5}	(0.66,1.73)
B	0.84	0.25	3.32	2.9×10^{-3}	(0.32,1.36)

Table 2-7 Two predictor model with factors A and C.

Y	**Coef.**	**St. Error**	**t**	**p-value**	**95 % CI**
A	2.00	0.05	36.62	6.73×10^{-22}	(1.90,2.12)
C	0.06	0.09	0.71	0.49	(-0.12,0.24)

Three factor model ($Y = f_{ABC}(A, B, C)$) is fit and the results are shown in Table 2-8. The p-value for the factor C (0.39) is greater than $\alpha_E = 0.01$. Hence C cannot be entered in the model and since there are no more factors are remaining, the stepwise selection process is stopped. Finally, the factors chosen are A and B which are both significant (Table 2-6).

Table 2-8 Three predictor model with factors A, B, and C.

Y	**Coef.**	**St. Error**	**t**	**p-value**	**95 % CI**
A	1.16	0.26	4.48	9.4×10^{-5}	(0.66,1.73)
B	0.84	0.25	3.31	2.9×10^{-3}	(0.32,1.36)
C	0.06	0.07	0.87	0.39	(-0.09,0.22)

2.6 Models for Olefin Polymerization Kinetics

The terminal model is commonly used to describe copolymerization reactions. In the terminal model, the rates of propagation depend on the type of monomer being polymerized *and* on the type of monomer last added to the polymer chain. Table 2-9 lists the elementary steps for the terminal model applied to binary olefin coordination copolymerization.

Table 2-9 Terminal model for binary olefin copolymerization.

Description	**Chemical Equation**	**Rate constant**
Propagation	$P_{r,A} + A \longrightarrow P_{r+1,A}$	$k_{p,AA}$
	$P_{r,B} + A \longrightarrow P_{r+1,A}$	$k_{p,BA}$
	$P_{r,A} + B \longrightarrow P_{r+1,B}$	$k_{p,AB}$
	$P_{r,B} + B \longrightarrow P_{r+1,B}$	$k_{p,BB}$
Transfer to hydrogen	$P_{r,A} + H_2 \longrightarrow P_H + D_{r,A}$	$k_{tH,A}$
	$P_{r,B} + H_2 \longrightarrow P_H + D_{r,B}$	$k_{tH,B}$
Transfer to monomer	$P_{r,A} + A \longrightarrow P_1 + D_{r,A}$	$k_{tM,AA}$
	$P_{r,B} + A \longrightarrow P_1 + D_{r,B}$	$k_{tM,BA}$
	$P_{r,A} + B \longrightarrow P_1 + D_{r,A}$	$k_{tM,AB}$
	$P_{r,B} + B \longrightarrow P_1 + D_{r,B}$	$k_{tM,BB}$
β hydride elimination	$P_{r,A} \longrightarrow P_H + D_{r,A}$	$k_{t\beta,A}$
	$P_{r,B} \longrightarrow P_H + D_{r,B}$	$k_{t\beta,B}$
Transfer to cocatalyst	$P_{r,A} + Al \longrightarrow P_1 + D_{r,A}$	$k_{tAl,A}$
	$P_{r,B} + Al \longrightarrow P_1 + D_{r,B}$	$k_{tAl,B}$

For copolymerization of monomers A and B, this requires four propagation rate constants (Table 2-9).

$$R_p = k_{p,AA}[P_{0,A}][A] + k_{p,BA}[P_{0,B}][A] + k_{p,AB}[P_{0,A}][B] + k_{p,BB}[P_{0,B}][B] \qquad (2.10)$$

where $[P_{0,A}]$ is the concentration of living chains terminated with monomer A, $[A]$ is the concentration of monomer A, $[P_{0,B}]$ is the concentration of living chains terminated with monomer B, $[B]$ is the concentration of monomer B, k_{PAA} is the rate constant of propagation

when monomer A is added to a living chain terminated with monomer *A*, k_{PAB} is the rate constant of propagation when monomer *B* is added to a living chain terminated with monomer *A*, k_{PBA} is the rate constant of propagation when monomer *A* is added to a living chain terminated with monomer *B*, and , k_{PBB} is the rate constant of propagation when monomer B is added to a living chain terminated with monomer B.

Equation (2.10) can also be written as,

$$R_p = [P_0][M]\,(f_A\,\emptyset_A\,k_{p,AA} + f_A\,\emptyset_B\,k_{p,BA} + f_B\,\emptyset_A\,k_{p,AB} + f_B\,\emptyset_B\,k_{p,BB}) \qquad (2.11)$$

where $\emptyset_A$ is the fraction of living polymer chains terminated with monomer *A*, $\emptyset_B$ is the fraction of living polymer chains terminated with monomer *B*, $[P_0]$ is the concentration living polymer chains terminated with monomer A *and* B, and $[M] = [A] + [B]$ is the total concentration of monomers.

By applying long chain approximation, $\emptyset_A$ can be calculated as,[16]

$$\emptyset_A = \frac{k_{PBA}\,f_A}{k_{PAB}\,(1 - f_A) + k_{PBA}\,f_A} \qquad (2.12)$$

$$\emptyset_B = 1 - \emptyset_A \qquad (2.13)$$

The pseudo-propagation rate constant is defined as,

$$\widetilde{k_p} = k_{PAA}\emptyset_A\,f_A + k_{PAB}\emptyset_A\,f_B + k_{PBA}\emptyset_B\,f_A + k_{PBB}\emptyset_B\,f_B \qquad (2.14)$$

The rate of propagation can be expressed in terms of the pseudo-propagation rate constant as,

$$R_p = \widetilde{k_p}[P_0][M] \qquad (2.15)$$

A similar approach can be applied to the rates of transfer to hydrogen, transfer to monomer, β hydride elimination, and transfer to cocatalyst.

Transfer to hydrogen,

$$R_{tH} = k_{tH,A}\left[P_{0,A}\right][H_2] + k_{tH,B}\left[P_{0,B}\right][H_2] \quad (2.16)$$

$$R_{tH} = [P_0][H_2]\,(k_{tH,A}\emptyset_A + k_{tH,B}\emptyset_B) \quad (2.17)$$

$$R_{tH} = \widetilde{k_{tH}}[P_0][H_2] \quad (2.18)$$

Transfer to monomer,

$$R_{tM} = k_{tM,AA}\left[P_{0,A}\right][A] + k_{tM,BA}\left[P_{0,B}\right][A] + k_{tM,AB}\left[P_{0,A}\right][B] + k_{tM,BB}\left[P_{0,B}\right][B] \quad (2.19)$$

$$R_{tM} = [P_0][M]\,(f_A\,\emptyset_A\,k_{tM,AA} + f_A\,\emptyset_B\,k_{tM,BA} + f_B\,\emptyset_A\,k_{tM,AB} + f_B\,\emptyset_B\,k_{tM,BB}) \quad (2.20)$$

$$R_{tM} = [P_0][M]\,\widetilde{k_{tM}} \quad (2.21)$$

β Hydride elimination,

$$R_{t\beta} = k_{t\beta,A}\left[P_{0,A}\right] + k_{t\beta,B}\left[P_{0,B}\right] \quad (2.22)$$

$$R_{t\beta} = [P_0]\,(\,k_{t\beta,A}\emptyset_A + k_{t\beta,B}\emptyset_B\,) \quad (2.23)$$

$$R_{t\beta} = \widetilde{k_{t\beta}}[P_0] \quad (2.24)$$

Transfer to cocatalyst,

$$R_{tAl} = k_{tAl,A}\left[P_{0,A}\right][Al] + k_{tAl,B}\left[P_{0,B}\right][Al] \quad (2.25)$$

$$R_{tAl} = [P_0][Al]\,(k_{tAl,A}\emptyset_A + k_{tAl,B}\emptyset_B) \quad (2.26)$$

$$R_{tAl} = \widetilde{k_{tAl}}[P_0][Al] \quad (2.27)$$

$$R_t = R_{tH} + R_{tM} + R_{t\beta} + R_{tAl} \tag{2.28}$$

Finally, the parameter τ defined as the ratio of total rate of termination to rate of propagation can be expressed as:

$$\tau = \frac{R_t}{R_p} = \frac{\widetilde{k_{tH}}[P_0][H_2]}{\widetilde{k_p}[M][P_0]} + \frac{\widetilde{k_{tM}}[P_0][M]}{\widetilde{k_p}[P_0][M]} + \frac{\widetilde{k_{t\beta}}[P_0]}{\widetilde{k_p}[P_0][M]} + \frac{\widetilde{k_{tAl}}[P_0][Al]}{\widetilde{k_p}[P_0][M]} \tag{2.29}$$

$$\tau = \frac{R_t}{R_p} = \frac{\widetilde{k_{tM}}[H_2]}{\widetilde{k_p}[M]} + \frac{\widetilde{k_{tM}}}{\widetilde{k_p}} + \frac{\widetilde{k_{t\beta}}}{\widetilde{k_p}[M]} + \frac{\widetilde{k_{tAl}}[Al]}{\widetilde{k_p}[M]} \tag{2.30}$$

The MWD of polyolefins made with single site catalysts can be described with Flory's most probable distribution,[16]

$$w(\log M) = 2.3026\ M^2\ \hat{\tau}^2 \exp(-M\hat{\tau}) \tag{2.31}$$

The parameter $\hat{\tau}$ is defined as,

$$\hat{\tau} = \frac{1}{M_n} = \frac{1}{r_n mw} = \frac{\tau}{mw} \tag{2.32}$$

$$mw = \overline{F_A} mw_A + (1 - \overline{F_A}) mw_B \tag{2.33}$$

where, mw is the average molecular weight of the repeat unit, $\overline{F_A}$ is the mole fraction of monomer *A* in the copolymer, mw_A is the molar mass of monomer *A*, and mw_B is the molar mass of monomer *B*. The average mole fraction of ethylene $\overline{F_A}$ in the copolymer can be calculated using the Mayo-Lewis equation as a function of the comonomer reactivity ratios ($r_A$and r_B) and molar fraction of monomer A and B in the reactor (f_A and f_B),

$$\overline{F_A} = \frac{(r_A - 1)f_A^2 + f_A}{(r_A + r_B - 2)f_A^2 + 2(1 - r_B)f_A + r_B} \tag{2.34}$$

3. Copolymer Synthesis and Characterization

3.1 Materials

The reagents used to synthesize the copolymers are listed in Table 3-1.

Table 3-1 Reagents used for polymer synthesis.

Reagent	Chemical Formula/Name	Assay	Manufacturer
Toluene	$C_6H_5CH_3$	99 %	Sigma-Aldrich
Ethylene	C_2H_4	99 %	Praxair
Hexene	C_6H_{12}	97 %	Sigma-Aldrich
Catalyst	Dimethylbis(cyclopentadienyl)silyl ZrCl2	98 %	Strem
MMAO-12	$[(CH_3)0.95(n\text{-}C_8)H_{17}]0.05AlO]_n$	N.A	Sigma-Aldrich
Nitrogen	N_2	99.999%	Praxair
Ethanol	C_2H_5OH	≥89.0%(GC)	Sigma-Aldrich
Triisobutylaluminum	$[(CH_3)_2CHCH_2]_3Al$	N.A	Sigma-Aldrich

N.A- Data unavailable

All polymers were made by solution polymerization. Toluene was used as the reaction medium. The polymerization runs were catalyzed with Me_2Cp_2Si-Zr (Figure 3-1) activated with MMAO-12.

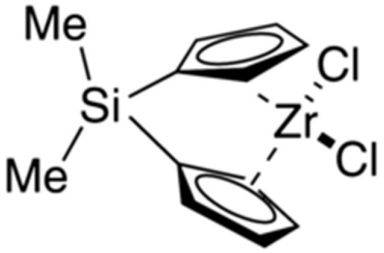


Figure 3-1 Molecular structure of dimethylbis(cyclopentadienyl)silyl $ZrCl_2$.[34]

3.2 Polymer Synthesis

A 300 ml Parr autoclave reactor was used to polymerize ethylene and 1-hexene in semi-batch mode. Ethylene was purified by flowing it through molecular sieves (3A/4A mixture) and copper (II) oxide beds to remove polar impurities before injection in the reactor (Figure 3-2). A Big Universal Trap and a Big Oxygen Trap removed polar impurities from nitrogen. Impurities were removed from the reactor by alternating purging it with nitrogen 10 times. A volume of 150 mL toluene and 0.5 g TIBA (as a scavenger) was charged into the reactor before heating it to 140 °C under continuous stirring at 1300 rpm for 15 minutes. The toluene-TIBA mixture was blown out of the reactor by pressurizing the reactor with nitrogen. Six more nitrogen purges removed any further impurities left. The reactor was left to cool to 30 °C before the reaction reagents were introduced. Glass vials (20 ml) sealed with rubber caps and metal crimps were used to prepare the catalyst solution in toluene, MMAO-12, and 1-hexene, inside the glovebox. The contents of the vials were transferred to the reactor under nitrogen pressure through stainless steel transfer needles. The molar ratio of Al to Ti in the reaction mixture was set to 20,000.

After charging toluene, MMAO-12, and 1-hexene, the stirrer was started, and temperature was set to the polymerization temperature. Once the set point temperature was achieved, ethylene was introduced until it saturated the solvent (no ethylene flow measured by the inline mass flow meter). The catalyst solution was charged (V-8, Figure 3-2) through a nitrogen differential pressure of 0.69 bar. The polymerizations were run for approximately 15 minutes. The on-off PID temperature controller (heating through an electrical band heater, Parr A2230HCEB, or cooling through VWR cooling tower MX07R-20-V11B) regulated the reactor temperature within ± 0.1 °C of the set point, except for the first 2 minutes after catalyst injection.

At the end of the polymerization, the stirrer was stopped, the temperature was set to 10 °C, the ethylene supply to the reactor was shut off, and the reaction mixture was purged out of the reactor under N_2 pressure. The polymer was then precipitated in 250 ml of ethanol, filtered, and dried in an oven at 70 °C overnight.

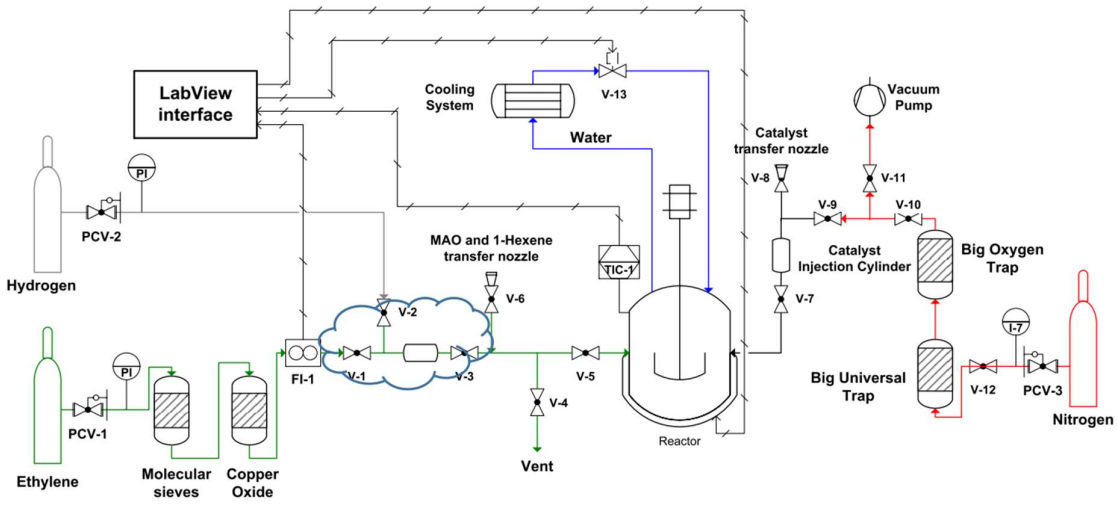


Figure 3-2 Reactor process flow diagram.[35]

3.3 Polyethylene Characterization

3.3.1 Gel Permeation Chromatography

A Polymer Char GPC unit with three linear columns (Agilent PLgel Olexis, 7.5 × 300 mm, 13 µm particles) and an infrared (IR4) detector was used to measure the MWD and SCB of the copolymers. Trichlorobenzene (TCB) was used as a solvent and continuous phase. All analyses were performed at 145 °C at a solvent flow rate of 1.0 ml/min. Polystyrene narrow standards were used to calibrate the GPC columns with the universal calibration curve. The Mark-Houwink constants used for polystyrene were $K = 1.9 \times 10^{-4}$ and $a = 0.655$, and for polyethylene were $K = 5 \times 10^{-4}$ and $a = 0.725$. An antioxidant, 2,6-di-tert-butyl-4-methylphenol, was added to TCB at a concentration of 300 ppm (by mass) to suppress degradation of TCB and polymer samples by oxidation.

The inline IR detector at the exit of the GPC columns functioned as a mass detector and also measured the SCB as a function of the polymer molecular weight. The IR signal, $A_{2965}(CH_3)/A_{2928}(CH_2)$, was calibrated using ethylene/1-hexene copolymer standards of known SCB. The SCB, measured in short chain branches per 1000 C atoms, can be converted to 1-hexene molar fraction, F_B, with the expression,

$$F_B = \frac{2 \times SCB}{1000 + (2 - n_c) \times SCB} \tag{3.1}$$

where n_c = 6 for 1-hexene.

3.3.2 Differential Scanning Calorimetry

A Mettler Toledo Star E DSC measured the thermograms of the dry copolymer samples (5-10 mg) in a 40 µl hermetic aluminum crucible. The sealed sample crucible and reference crucible were placed on the heaters, and the thermograms were measured in the range from 20 °C to 160 °C. The second melting scan was used to determine the melting peak temperatures. The heating rate used was 10 °C/min.

4. Results and Discussion

4.1 Experimental Design

The ethylene/1-hexene copolymers were synthesized following the IV optimal design described in Section 2.3. The levels for temperature, 1-hexene/ethylene ratio, and ethylene concentration were chosen so that they covered a range of commercial importance (Table 4-1).

Table 4-1 Experimental factor ranges.

Factor Name	Code	Min	Max	Mean	SD
Temperature (^{o}C)	T	110	130	120	7.7
1-Hexene/ethylene ratio	R	0	0.8	0.43	0.3
Ethylene concentration (mol/L)	E	0.34	0.86	0.6	0.2

The factor values can be visualized using pairwise scatter plots in Figure 4-1. The IV optimal design included points on the edges, centroid, and replicates to span the experimental space and quantify the pure error in the system. Table 4-2 shows the conditions for all experiments. Highlights of different colors identify replicate runs.

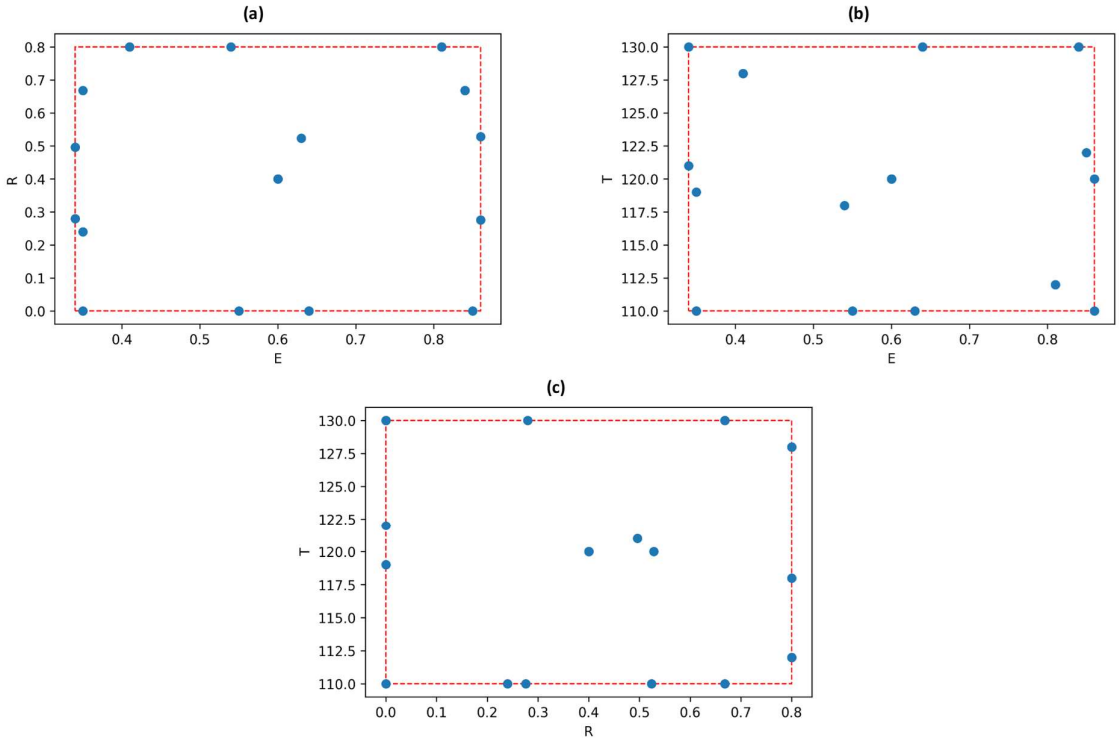


Figure 4-1 Design points in experimental space: a) R × E, b) T ×E, c) T × R.

Table 4-2 IV Optimal design of experiments.

ID	Run	E	R	T
0	1	0.60	0.400	120
4	2	0.63	0.524	110
13	3	0.34	0.280	130
15	4	0.64	0.000	130
12	5	0.41	0.800	128
10	6	0.34	0.496	121
0	7	0.60	0.400	120
5	8	0.35	0.668	110
6	9	0.81	0.800	112
14	10	0.84	0.668	130
3	11	0.86	0.276	110
8	12	0.35	0.000	119
14	13	0.84	0.668	130
15	14	0.64	0.000	130
1	15	0.55	0.000	110
2	16	0.35	0.240	110
12	17	0.41	0.800	128
11	18	0.85	0.000	122
0	19	0.60	0.400	120

7	20	0.54	0.800	118
6	21	0.81	0.80	112
9	22	0.86	0.528	120

It is not unusual for RSM models to overfit the training data. If the empirical model cannot predict well data points not used during the fitting procedure, its ultimate purpose is lost. Therefore, it is important to validate the model within the bounds of the training data with experiments that were not included to train the model. Hence, four validation data points (V1 to V4, listed in Table 4-3) were placed in the gaps of the input factor space, as shown in Figure 4-2. Polymerizations for these conditions were performed and the products were analyzed for MWD, SCB, and melting temperature. The execution of the experimental design was done by Dr. Paul DesLauriers.

Table 4-3 Conditions for the validation polymerizations.

Run	**E**	**R**	**T**
V1	0.5	0.6	125
V2	0.7	0.6	115
V3	0.5	0.2	115
V4	0.7	0.2	125

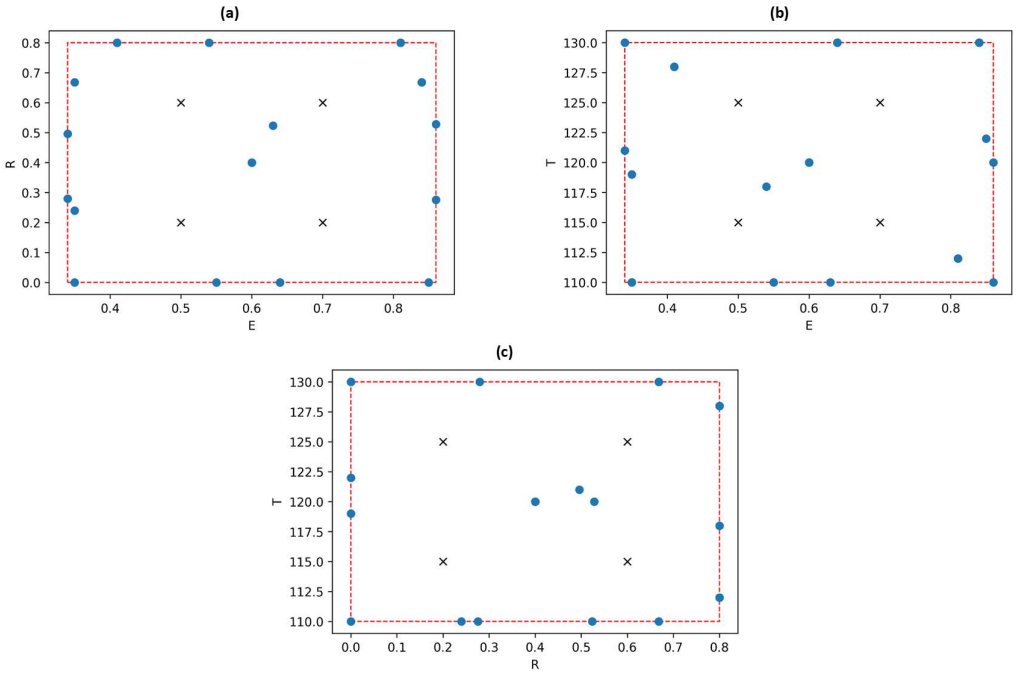


Figure 4-2 Validation runs (X) in the experimental space: a) R × E, b) T × E, c) T × R.

4.2 Modeling Polyethylene Microstructure

4.2.1 Molecular Weight Averages

Even though the most important microstructural distribution of a polymer population is its MWD, molecular weight averages are more readily grasped and easier to use than the MWD itself. Molecular weight averages, such as M_n and M_w, are often used to differentiate between different polyethylene samples, but they may not be enough to unequivocally characterize them.

A generalized second order polynomial was used to model how $\log M_w$ depended on the three factors listed in Table 4-1. The stepwise regression algorithm was used to determine statistically significant factors that explained the variation in the measured $\log M_w$ values. The lack of fit test was insignificant for the RSM model for $\log M_w$ (Table 4-6). The parity plot contrasting measured $\log M_w$ and predicted $\log M_w$ is shown in Figure 4-3. The data is scattered along both sides of the $x = y$ line, suggesting that the residuals are randomly distributed. The validation runs are also included in Figure 4-3. The predicted R^2 for the

M_w model is 0.71. The R^2 and R^2_{adj} are 0.93 and 0.91 respectively. The RSM model for M_w is,

$$\log M_w = a + b\,T^2 + c\,R + d\,ET + e\,E^2 \tag{4.1}$$

where $a = 4.250, b = -3.022 \times 10^{-5}, c = -0.096, d = 0.005$, and $e = -0.358$.

Table 4-4 Measured and predicted molar masses for the DoE and validation runs.

Run	$M_{w,exp}$	$M_{n,exp}$	$M_{w,pred}$
1	9800	4900	9500
10	9000	4000	8500
11	11300	5700	10600
12	10200	4500	9200
13	9200	4200	8500
14	9800	4600	9300
15	12100	5000	10900
17	7500	3500	7600
18	11400	5800	10200
19	10200	5100	9500
2	10900	5400	10100
20	9400	4300	8800
21	10200	4800	9500
22	9300	4300	9400
3	7800	3500	7700
4	9500	3800	9300
5	7600	4200	7600
6	8100	3800	8200
7	9700	4800	9500
8	8500	4000	8900
9	10400	5000	9500
16	10000	5400	9600
V1	9000	4300	8600
V2	10800	4800	10200
V3	11000	4800	10500
V4	10300	4500	10200

$M_{w,exp}$: M_w measured by GPC

$M_{w,pred}$: M_w predicted with Equation (4.1)

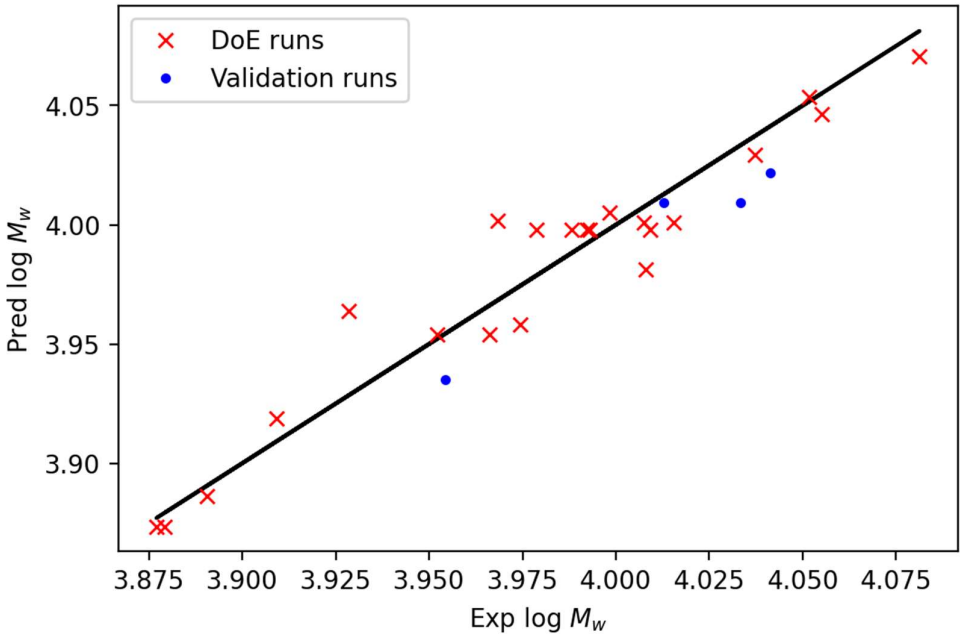


Figure 4-3 Parity plot for log M_w.

Table 4-5 Regression table for the RSM model for **log M_w**.

log M_w	**Coef.**	**St. Error**	**t**	**p-value**	**95 % CI**
T^2	-3.022 x 10^{-5}	3.55 x 10^{-6}	-8.5	***	(-3.770 x 10^{-5},-2.770 x 10^{-5})
R	-0.096	0.013	-7.7	***	(-0.123, -0.070)
ET	0.005	0.001	4.2	***	(0.002,0.007)
E^2	-0.358	0.115	-3.1	***	(-0.601, -0.115)
Constant	4.250	0.030	140	***	(4.186,4.314)
R^2	0.93	**F-value**	53.9	**df (model)**	4
R^2_{adj}	0.91	**p-value**	***	**df (residuals)**	17

*** p < 0.01, ** p < 0.05, * p < 0.1

Table 4-6 ANOVA table for the RSM model for log M_w.

Source	**Sum of squares**	**df**	**F-value**	**p-value**	**Significance**

Model	0.061	4	53.9	<0.001	Significant
T^2	0.021	1	72.6	<0.001	Significant
R	0.017	1	59.2	<0.001	Significant
ET	0.005	1	17.6	<0.001	Significant
E^2	0.003	1	9.6	0.006	Significant
Residual	0.005	17	-	-	
Lack of fit	0.004	11	5.11	0.03	Not significant*
Pure error	0.0005	6	-	-	-

df: degrees of freedom
level of significance α = 0.01

The directional performance of the model can be assessed by evaluating how log M_w varies as a function of two input factors while keeping the third one constant. These results are plotted in Figure 4-4 .

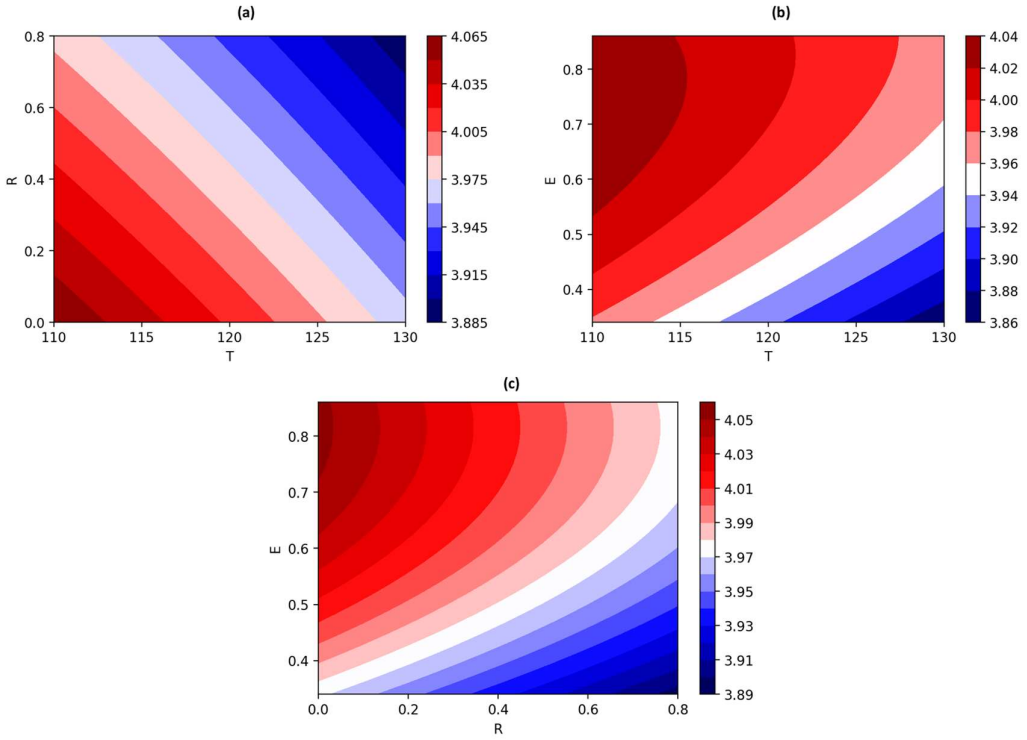


Figure 4-4 Effect of factors on log M_w: a) R × T at E = 0.5 mol/L, b) E × T at R = 0.5, c) E × R at T = 120 ºC.

Figure 4-4.a shows that M_w increases when the temperature and 1-hexene/ethylene ratio decreases since the ratio of the propagation to the chain transfer rates increases. Likewise, Figure 4-4.b shows that M_w increases when the ethylene concentration increases (increasing propagation rate) and the temperature decreases (decreasing transfer-to-propagation ratio). Finally, Figure 4-4. c shows that M_w increases at high ethylene concentrations and lower 1-hexene concentrations, since the transfer-to-propagation ratio decreases under these conditions. These findings agree with the accepted mechanism for olefin polymerization with coordination catalysts.

4.2.2 MWD Prediction

Modeling MWD is an extension of the case of modeling M_w. For polyolefins made with a single site catalyst, the MWD is given by Equation (2.31), which is repeated below for convenience's sake,

$$w(\log M) = 2.3026\ M^2\ \hat{\tau}^2 \exp(-MW\ \hat{\tau}) \tag{4.2}$$

Where,

$$\hat{\tau} = \frac{1}{M_n} = \frac{1}{r_n mw} = \frac{\tau}{mw} \tag{4.3}$$

$$mw = \overline{F_A} mw_A + (1 - \overline{F_A}) mw_B \tag{4.4}$$

$$\tau = \frac{R_t}{R_p} = \frac{\widetilde{k_{tH}}[H_2]}{\widetilde{k_p}[M]} + \frac{\widetilde{k_{tM}}}{\widetilde{k_p}} + \frac{\widetilde{k_{t\beta}}}{\widetilde{k_p}[M]} + \frac{\widetilde{k_{tAl}}[Al]}{\widetilde{k_p}[M]} \tag{4.5}$$

Theoretical value of dispersity of polymers synthesized with co-ordination catalyst which are single site in nature is equal to 2.[16] The dispersity (Đ) is defined as the ratio of M_w to M_n. Hence for such polymers:

$$Đ = \frac{M_w}{M_n} = 2 \tag{4.6}$$

From Equation (4.6), M_w can be expressed as:

$$M_w = 2\,M_n \tag{4.7}$$

We showed above that M_w could be predicted adequately with Equation (4.1). We will now extend his approach to model the complete MWD by discretizing it into several narrow slices centered on distinct molecular weights along the distribution as shown in Figure 4-5. The area of each slice is the mass fraction of polymer chains with molecular weights that fall within that range.

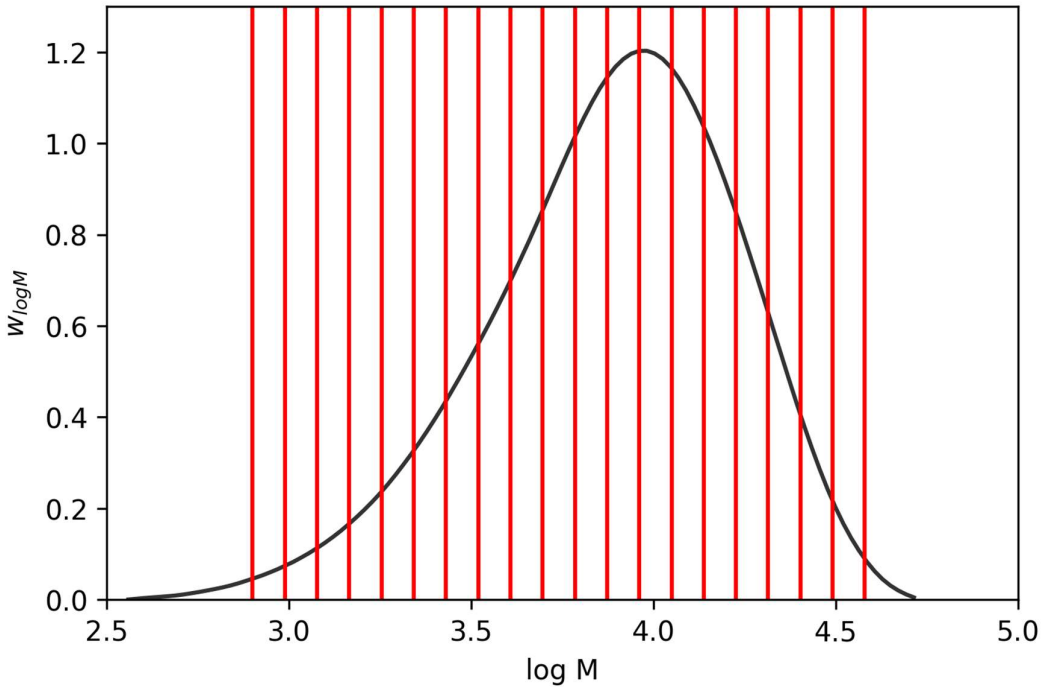
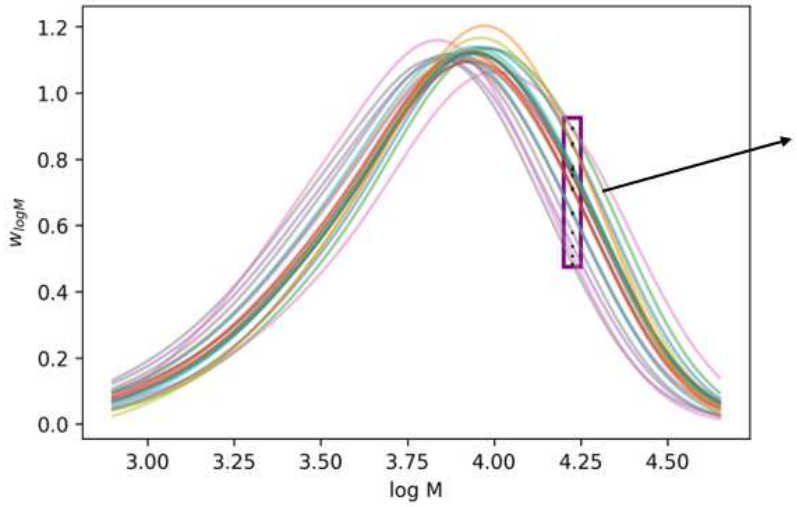


Figure 4-5 Illustrative log M slices.

The same approach applied to model M_w was applied to the central points of 100 MWD slices. The resulting set of RSM models were then used to predict the MWDs of the polymers made in the validation runs to assess how well this modeling approach described the polymer MWD. The MWD was discretized into 100 slices in the log M scale, from log M = 2.9 to log M = 4.65. This range was chosen to satisfy the condition,

$$\forall\, M, w_{log\,M} \geq 0.005 \tag{4.8}$$

The height of MWD for the DoE runs for a distinct molecular weight is shown in Figure 4-6. The discretization range imposed by Equation (4.8) truncated the low and high molecular weight shoulders of the MWD. Since these tails have low signal to noise ratio, this allowed us to model the profile in the range where the responses were more significant. The data lost by applying Equation (4.8) was recovered by applying the tail approximation method discussed in Section (4.2.3).



Run #	$w_{log\,M}$	E	T	R
1	0.749528	0.60	120.0	0.400
2	0.845684	0.63	110.0	0.524
3	0.537679	0.34	130.0	0.280
4	0.713048	0.64	130.0	0.000
5	0.507815	0.41	128.0	0.800
6	0.579697	0.34	121.0	0.496
7	0.767245	0.60	120.0	0.400
8	0.637753	0.35	110.0	0.668
9	0.770392	0.81	112.0	0.800
10	0.634514	0.84	130.0	0.668
11	0.891364	0.86	110.0	0.276
12	0.749998	0.35	119.0	0.000
13	0.638893	0.84	130.0	0.668
14	0.754584	0.64	130.0	0.000
15	0.894405	0.55	110.0	0.000
16	0.848110	0.35	110.0	0.240
17	0.484484	0.41	128.0	0.800
18	0.842032	0.85	122.0	0.000
19	0.780030	0.60	120.0	0.400
20	0.706980	0.54	118.0	0.800
21	0.772266	0.81	112.0	0.800
22	0.713089	0.86	120.0	0.528

Figure 4-6 Discretization of log *M* space.

Lack of fit test determines if a large proportion of the residual SSE is due to lack of model fit for a regression model. The residual sum of squared error (SSE) is comprised of sum of squares of lack of model fit (SSLF) and pure error sum of squares (SSPE).

$$SSE_{residual} = SSLF + SSPE \tag{4.9}$$

SSLF and SSPE can be calculated as:

$$SSLF = \sum_{k=1}^{c}\sum_{j=1}^{n} \left(\overline{y_k} - \widehat{y_{kj}}\right)^2 \tag{4.10}$$

$$SSPE = \sum_{k=1}^{c}\sum_{j=1}^{n} \left(y_{kj} - \overline{y_k}\right)^2 \tag{4.11}$$

where, $\overline{y_k}$ is the average of measured values of response for k[th] distinct run, $\widehat{y_{kj}}$ is the predicted value of response for k[th] distinct run and j[th] data point, y_{kj} is the measured value of response for k[th] distinct run and j[th] data point, c is the number of distinct runs, and n is the number of data points. The mean sum of squares of lack of model fit and pure error can be calculated as:

$$MSLF = \frac{SSLF}{df_{lf}} \tag{4.12}$$

$$MSPE = \frac{SSPE}{df_{pe}} \tag{4.13}$$

Where, df_{lf} is the degrees of freedom of lack of fit and df_{pe} is the degrees of freedom of pure error. The df_{lf}, and df_{pe} are:

$$df_{lf} = c - 1 - df_{model} \tag{4.14}$$

$$df_{pe} = n - c \tag{4.15}$$

where df_{model} is the number of terms in the model (not including the intercept). The F statistic for lack of fit is calculated as:

$$F^* = \frac{MSLF}{MSPE} \tag{4.16}$$

The F^* is compared to the critical F-value from the F- distribution with df_{lf} numerator degrees of freedom and df_{pe} denominator degrees of freedom($F(1-\alpha, df_{lf}, df_{pe})$). The null and alternative hypothesis test for the lack of fit test is: a) H_0 (Null hypothesis): The lack of fit is not significant, b) H_1 (Alternative hypothesis): The lack of fit is significant. The lack of fit tests accept H_0 except in 3.9783≤ log M ≤ 4.0136 and 4.4732≤ log M ≤ 4.6500 (Figure 4-7 and Appendix C: Lack of Fit Tests). The level of significance used was α= 0.01.

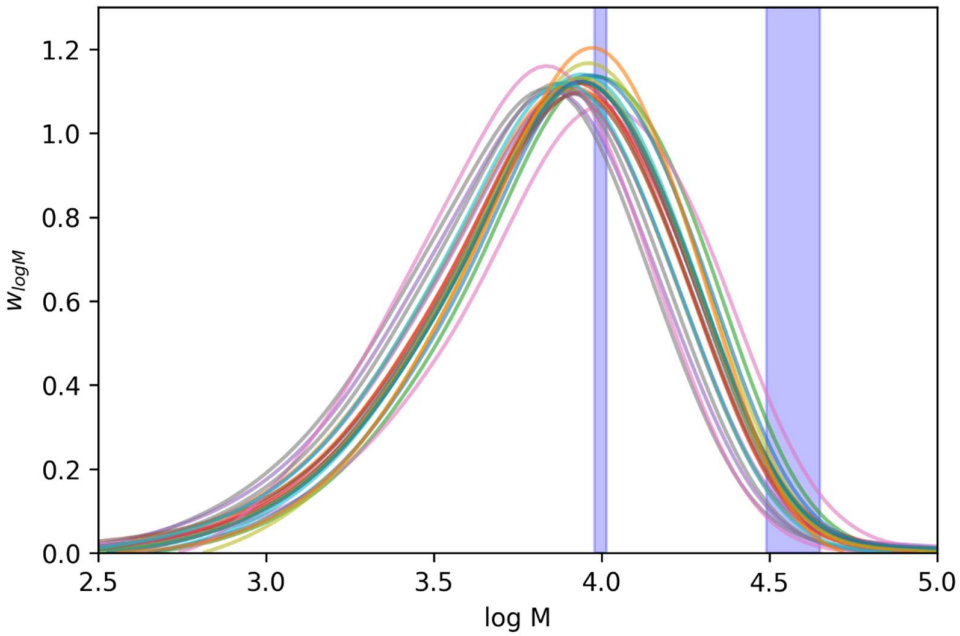


Figure 4-7 Slices where the lack of fit is significant.

The F-test of the overall significance of regression compares the regression model to an intercept only model, i.e., a model with no terms (predictors).[36] The null and alternate hypotheses for the F-test of the overall significance are: a) H_0 (Null hypothesis): The model is insignificant, b) H_1 (Alternative hypothesis): The model is significant. The F statistic for overall significance of regression can be calculated as:

$$F^{os} = \frac{ESS/df_{model}}{SSE_{residual}/(n - df_{model} - 1)} \tag{4.17}$$

where, ESS is the explained sum of squares (or the model sum of squares) and $SSE_{residual}$ is the error sum of squares. The F^{os} is compared to the critical F-value from the F- distribution with df_{model} numerator degrees of freedom and $n - df_{mode} - 1$ denominator degrees of freedom($F(1-\alpha, df_{model}, n - df_{model} - 1)$). The F-tests reject H_0 with the one exception. In the range $3.8368 \leq \log M \leq 3.9782$ (Figure 4-8 and Appendix D: Regression and ANOVA Tables), the stepwise selection returns an intercept only model where the intercept is equal to the mean of the response. F- ratio in this case is undefined, hence the F-test is not applicable. The level of significance used was α= 0.01.

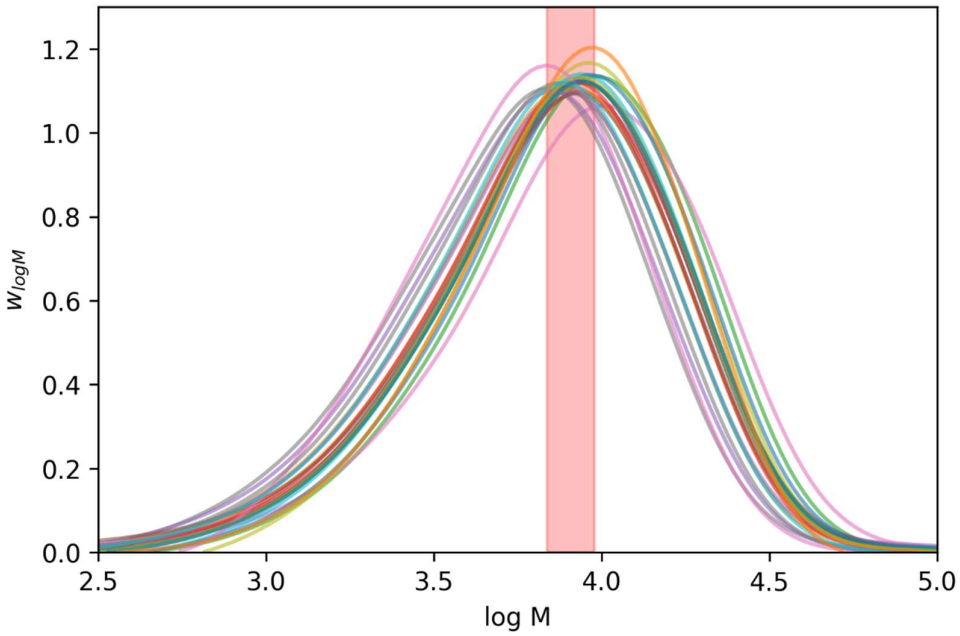


Figure 4-8 Slices with intercept only models.

The RSM models were accepted if the model satisfied the following criteria: a) F-test for the overall significance of regression concluded that the model was significant, b) F-test for lack of fit concluded that the lack of fit was insignificant. All the models built in this project were tested for this acceptance criteria. The $\log M$ regions that satisfied both the conditions were $2.9 \leq \log M < 3.8368$ and $4.0136 < \log M < 4.4732$.

4.2.3 Tail Approximation

Applying the condition in Equation (4.8) led to losing the information in the low M tail ($\log M$ <2.9) and the high M tail ($\log M$ >4.65). Although the mass percentages in the low M and high M tails are lower than 2.57 % and 1.5 %, they greatly influence the molar mass averages M_w and M_n. The low M tail strongly influences the M_n and the high M tail strongly influences M_w. The mass percentages of polymer in low and high M tails are shown in Table 4-7.

Table 4-7 Mass percentages of polymer in low and high M tails.

Run#	$\log M < 2.9$	$\log M > 4.65$
Run-1	0.89	0.62
Run-2	0.51	0.91
Run-3	2.53	0.16
Run-4	2.57	0.68
Run-5	0.48	0.09
Run-6	1.91	0.16
Run-7	0.98	0.56
Run-8	1.7	0.23
Run-9	0.93	1.03
Run-10	1.91	0.72
Run-11	0.41	0.77
Run-12	1.54	1.05
Run-13	1.75	1.34
Run-14	1.25	0.73
Run-15	1.61	1.5
Run-16	0.5	0.05
Run-17	2.28	0.3
Run-18	0.07	1.1
Run-19	0.62	0.75
Run-20	1.61	0.59
Run-21	1.16	0.76
Run-22	1.66	0.35

RSM modeling the MWD allows to model the profile in the region that accounts for more than 96.75 % mass of the polymer. However, it still does not allow baseline to baseline modeling of the MWD. The regions with unacceptable RSM models were estimated by deconvoluting the rest of the RSM modeled MWD.

The steps involved in “tail approximation” explained through an example of Run-19 are:

- Construct the MWD predicted with the RSM approach based on the acceptance criteria discussed in Section 4.2.2, as shown in Figure 4-9.

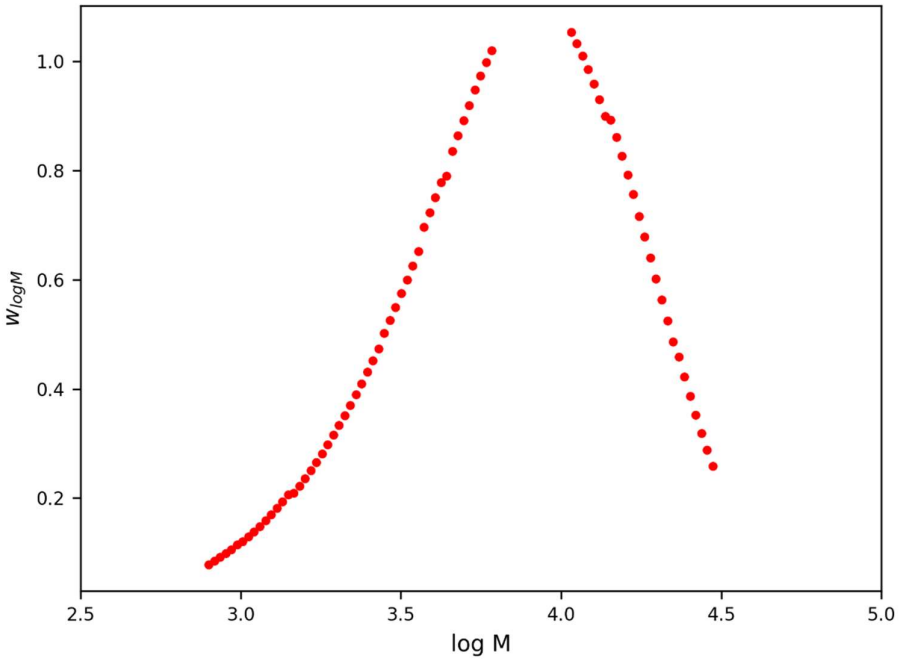


Figure 4-9 RSM Modeled MWD profile.

- Deconvolute the modeled MWD shown in Figure 4-9 using the equation[37,38]

$$w_{log\,M} = \sum_{j=1}^{n} m_j (2.3026 \times {M_i}^2 {\hat{\tau}_j}^2 \exp(-M_i {\hat{\tau}_j}^2)) \tag{4.18}$$

$$\hat{\tau} = \frac{1}{M_n} = \frac{1}{r_n m w} = \frac{\tau}{mw} \tag{4.19}$$

The minimum number of Flory's distributions (n) required to describe the RSM-modeled MWD is obtained by minimizing the objective function,

$${\chi_1}^2 = \sum_{i=1}^{n_{RSM}} (w_{\log M,i}^{\mathrm{RSM}} - w_{\log M,i})^2 \tag{4.20}$$

$$\chi_1{}^2 = \sum_{i=1}^{n_{RSM}} [\, w_{\log M,i}^{\mathrm{RSM}} - \sum_{j=1}^{n} m_j (2.3026 \times M_i{}^2 \hat{\tau}_j{}^2 \exp(-M_i \hat{\tau}_j))]^2 \tag{4.21}$$

where n_{RSM} is the number of data points in the RSM modeled MWD, and $\chi_1{}^2$ is the sum of the squares of the differences between the RSM MWD data points and modeled values. $\chi_1{}^2$ is minimized by choosing the minimum number of Flory's distributions by optimizing mass fractions of polymer populations for site type *j*, m_j, and $\hat{\tau}_j$ by estimating 2 × *n*-1 parameters (since, $\sum m_j = 1$). Deconvolution was done with 2 and 3 Flory's distributions (Appendix B: 2-site and 3-site Deconvolution). 2 Flory's distributions were chosen as it described the MWD just the same as 3 sites.

- The Flory's distribution parameters are used to obtain MWD (Figure 4-10).

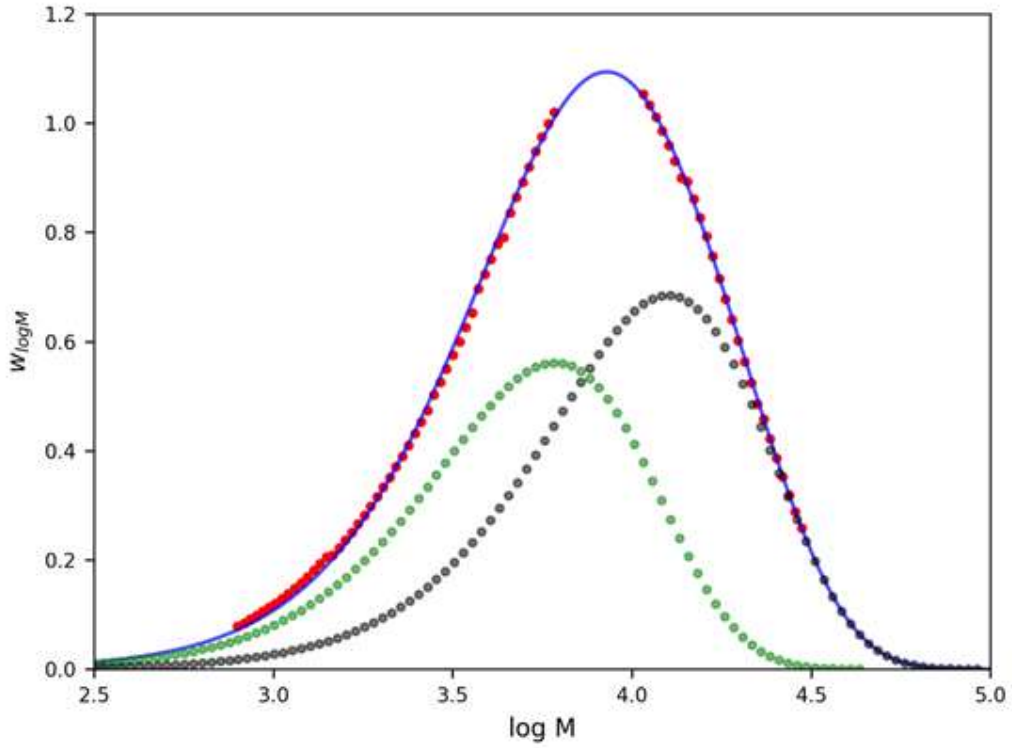


Figure 4-10 Tail approximation for Run-19.

The average SSE for 2-site and 3-site fits were comparable(Figure 4-12), the average for SSE 3-site fit was only 3.3 % lower than that for 2-sites (Appendix B: 2-site and 3-site

Deconvolution). The 3-site fits for 6 runs (Runs 1,2, 11, 18, 19, and 20) resulted in one extremely high $M_w$site ($\sim$ 100 million) with a small mass fraction (in the range 0.01-0.03 g/g). This clearly, is unlikely to be a realistic description of the MWD. The 3-site fit has 5 independent parameters that can be tuned to fit the MWD, while the 2-site fit has 3 independent parameters. The extremely high molecular weight sites are the artifacts of overfitting. In Run-15, the 3-site fits returned identical values of M_w for two sites (Appendix B: 2-site and 3-site Deconvolution). This shows that the 3-site model is over specified. As the fits with 2 and 3 sites were comparable (shown in Figure 4-12), choosing 2 sites represents the choice of minimum parameters to describe MWD. Hence, the 2-sites fits were used for tail approximation.

Both the 2-site and 3-site fits resulted in high bias in predicting the MWD in the range log M < 2.9 and log M > 4.47 (Figure 4-11). It is important to note that the fits for 2 and 3 sites were performed on the RSM model predicted points and not on the tails, the tails were predicted from the fits.

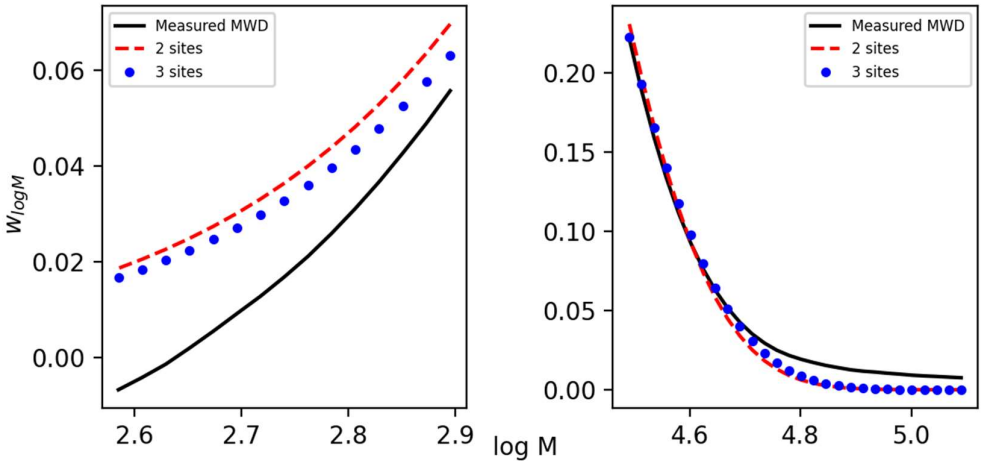


Figure 4-11 MWD tail approximation.

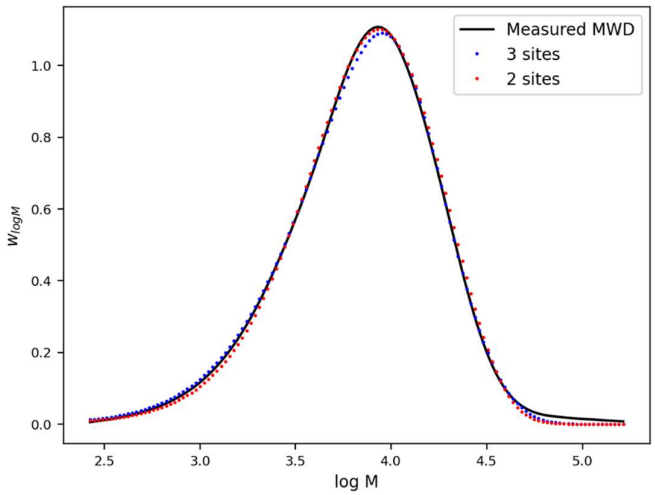


Figure 4-12 Deconvolution fits with 2 and 3 sites.

4.2.4 The Dovetail Process

The dovetail process works like a dovetail joint, hence the name. A dovetail joint has two parts: a tail and a pin. The dovetail process similarly has two parts: a) the RSM model predictions (like the tail), and b) the tail approximation (like the pin), shown in Figure 4-14. The process starts by predicting the MWD in the log M region where the RSM models are acceptable. This procedure generates most of the MWD and forms the basis to perform the tail approximation. The tail approximation takes the RSM-predicted MWD and fits it to an appropriate number of Flory's distributions. These distributions are further used to estimate the MWD profile in the log M region wherein the RSM models are unacceptable.

The dovetail process predicts the complete MWD, baseline to baseline. The tail approximation acts a filler (pins that wedge into the tails, using the dovetail joint analogy shown in Figure 4-13).

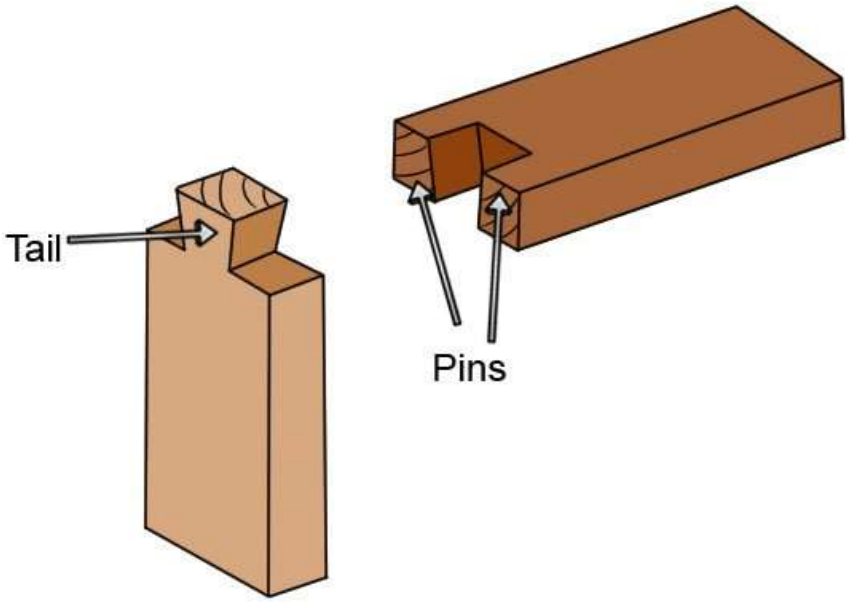


Figure 4-13 Dovetail joint with tails and pins.[39]

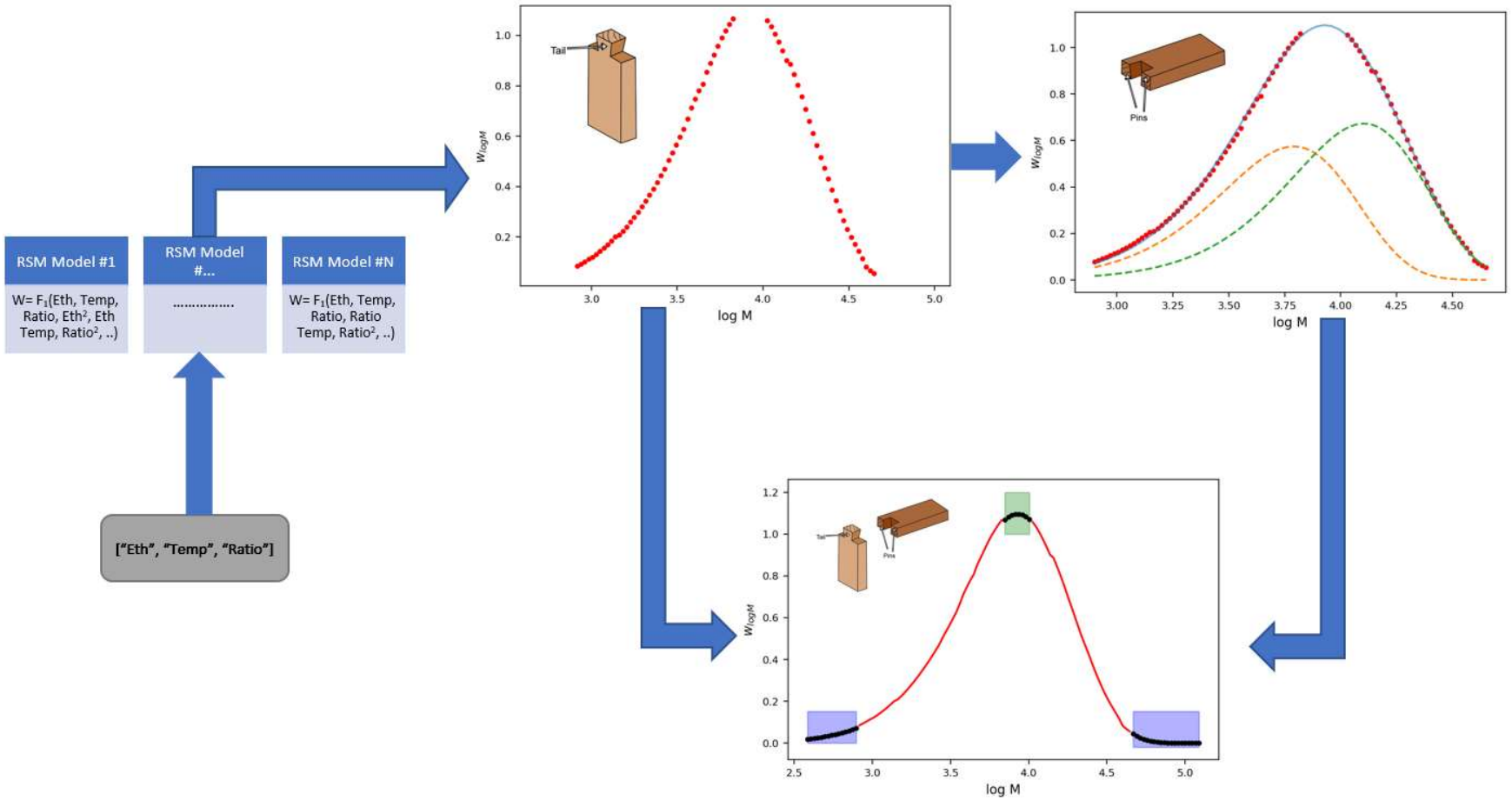


Figure 4-14 Illustration of the dovetail process.[39]

4.2.5 Performance on Training data

The dovetail process was applied to all the DoE runs and the overlay plots of measured and predicted MWD are shown in Figure 4-15. Once complete baseline to baseline predictions for all training runs are made, the molecular weight averages M_w, M_n, M_z, and M_{z+1} can be calculated from the predicted MWD (Table 4-8). The values A1, B1, and C1 (Table 4-8) did not make any physical meaning as the measured MWD of the runs 13 and 7 have negative values on the low and high M tails. The parity plots of M_w, M_n, M_z, and M_{z+1} are shown in Figure 4-16 to Figure 4-19.

The scatter of most of the runs below the parity line (Figure 4-16) indicates that M_w calculated from the predicted MWD are underpredictions. This is explained by the underprediction in the $\log M > 4.47$, as shown in Figure 4-11. Scatter on both sides of the parity line is observed in Figure 4-17. Higher underprediction of M_n occurs as M_n increases (Figure 4-17). High levels of scatter substantially below the parity line ($x = y$ line) in Figure 4-18 and Figure 4-19 indicates underprediction of M_z and M_{z+1}. This is also explained by the underprediction of the high molecular weight tail, as shown in Figure 4-11. The degree of underprediction is higher in the case of M_z and M_{z+1} as compared to M_w because they are higher moments of the MWD. The high molecular weight tail strongly influences the values of M_z and M_{z+1}.

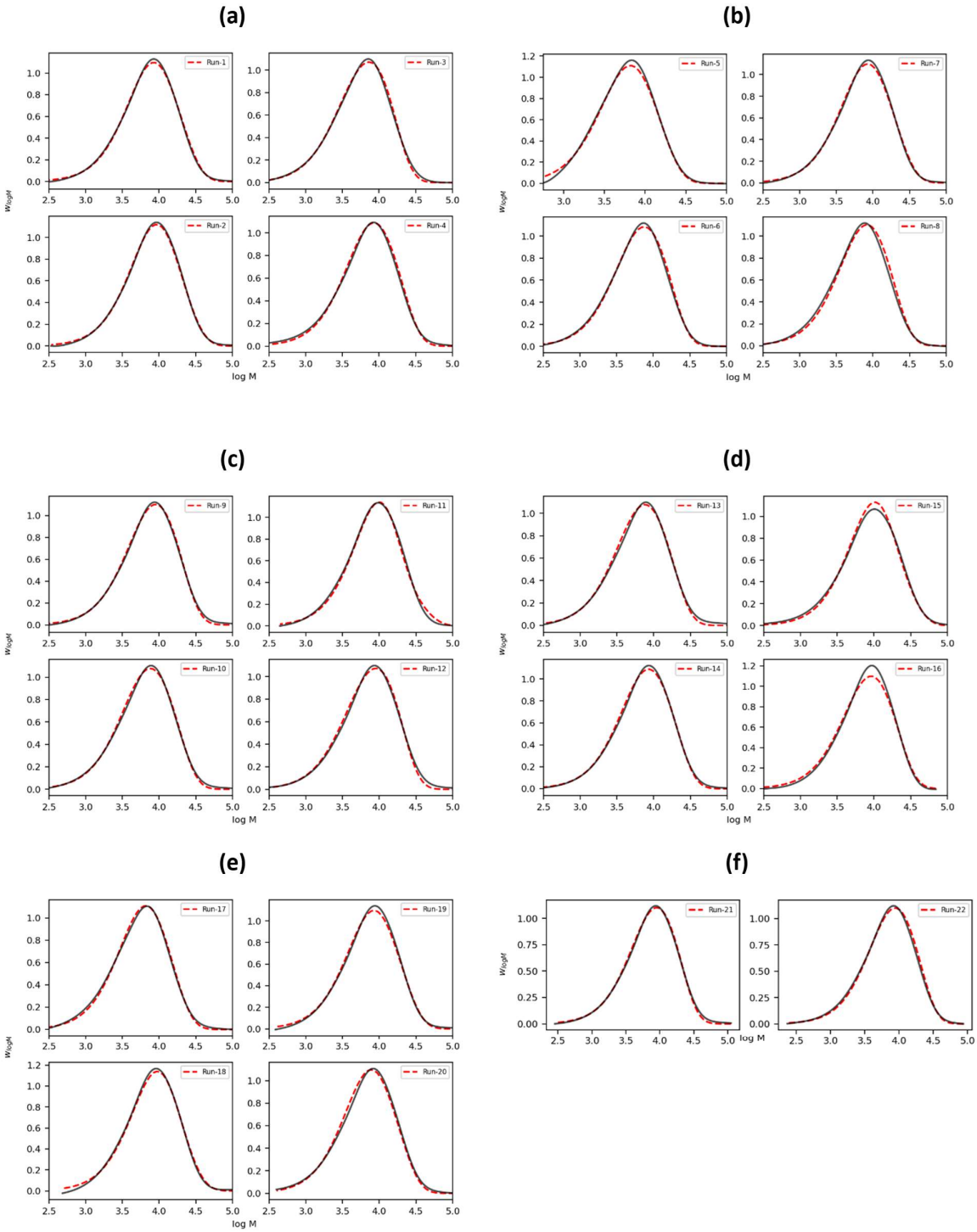


Figure 4-15 Overlay plots: a) runs 1-4, b) runs 5-8, c) runs 9-12, d) runs 13-16, e) runs-17-20, f) runs 21 and 22.

Table 4-8 Molar mass averages prediction on DoE runs.

Run#	M_w^{exp}	M_n^{exp}	$Đ^{exp}$	M_z^{exp}	M_{z+1}^{exp}	M_w^{pred}	M_n^{pred}	$Đ^{pred}$	M_z^{pred}	M_{z+1}^{pred}	R^2
1	9800	4900	2.01	17200	28100	9700	4600	2.13	16200	23400	0.999
2	10900	5400	2.01	19600	36000	10500	5100	2.06	17500	25200	0.999
3	7800	3500	2.20	13000	16600	7600	3500	2.17	12300	17000	0.998
4	9500	3800	2.48	17300	28400	9400	4400	2.16	15500	21900	0.997
5	7600	4200	1.82	12000	15100	7300	4000	1.85	12000	17000	0.996
6	8100	3800	2.11	13600	19700	8100	3800	2.11	13300	18600	0.998
7	9700	4800	2.02	14500	C1	9700	4600	2.10	16200	23600	0.999
8	8500	4000	2.10	13000	8700	9000	4200	2.12	14500	20300	0.994
9	10400	5000	2.09	20300	37200	9600	4600	2.11	15500	21600	0.999
10	9000	4000	2.22	17400	34600	8400	3900	2.15	13800	19500	0.998
11	11300	5700	1.97	18800	28200	11800	5700	2.07	21000	33300	0.997
12	10200	4500	2.29	19300	35200	9300	4400	2.14	15200	21000	0.997
13	9200	4200	2.23	A1	B1	8400	4000	2.11	13800	19500	0.998
14	9800	4600	2.13	16400	17800	9400	4400	2.14	15500	21900	0.998
15	12100	5000	2.43	21500	31500	11900	5500	2.14	20100	29800	0.995
16	10000	5400	1.85	15100	19800	9900	4700	2.11	16000	22300	0.992
17	7500	3500	2.14	13400	21000	7300	3600	2.05	12000	17000	0.998
18	11400	5800	1.94	31500	137400	10500	5300	1.97	17200	24700	0.998
19	10200	5100	2.00	18400	32800	9700	4700	2.05	16200	23300	0.997
20	9400	4300	2.18	16600	26500	8900	4400	2.02	14800	21200	0.995
21	10200	4800	2.12	18300	31000	9600	4600	2.08	15500	21600	0.999
22	9300	4300	2.15	15700	23500	9400	4500	2.11	15300	21400	0.997

A1=-22100, B1=2272000, C1=-5900

$Đ$: Dispersity calculated by the ratio of M_w to M_n

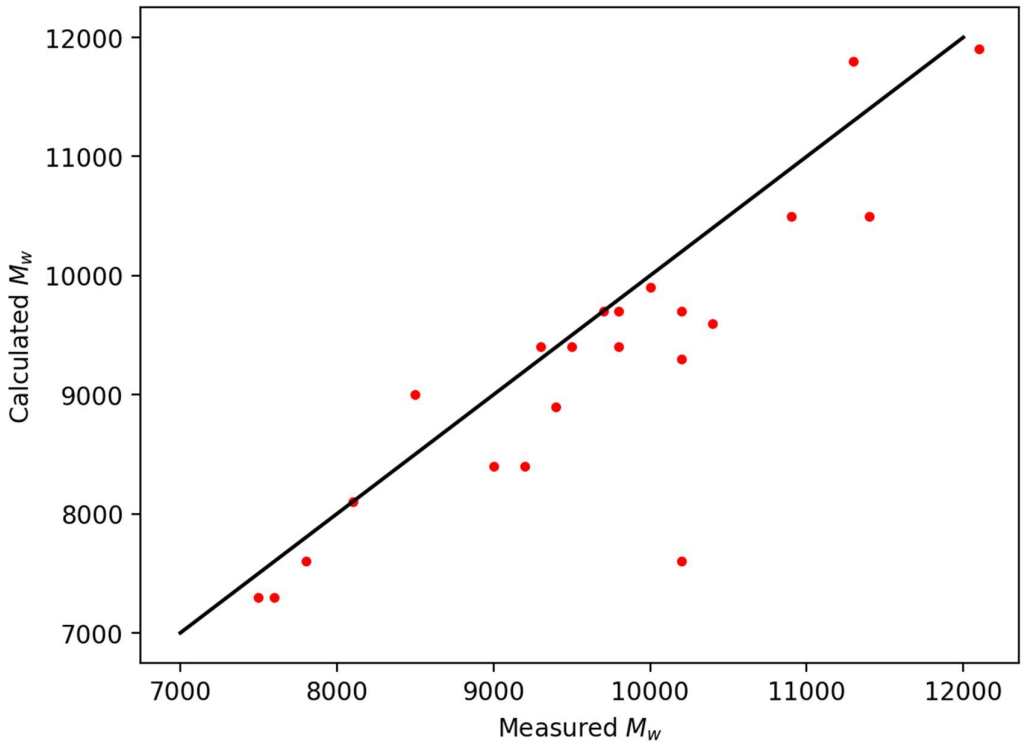


Figure 4-16 Parity plot of M_w.

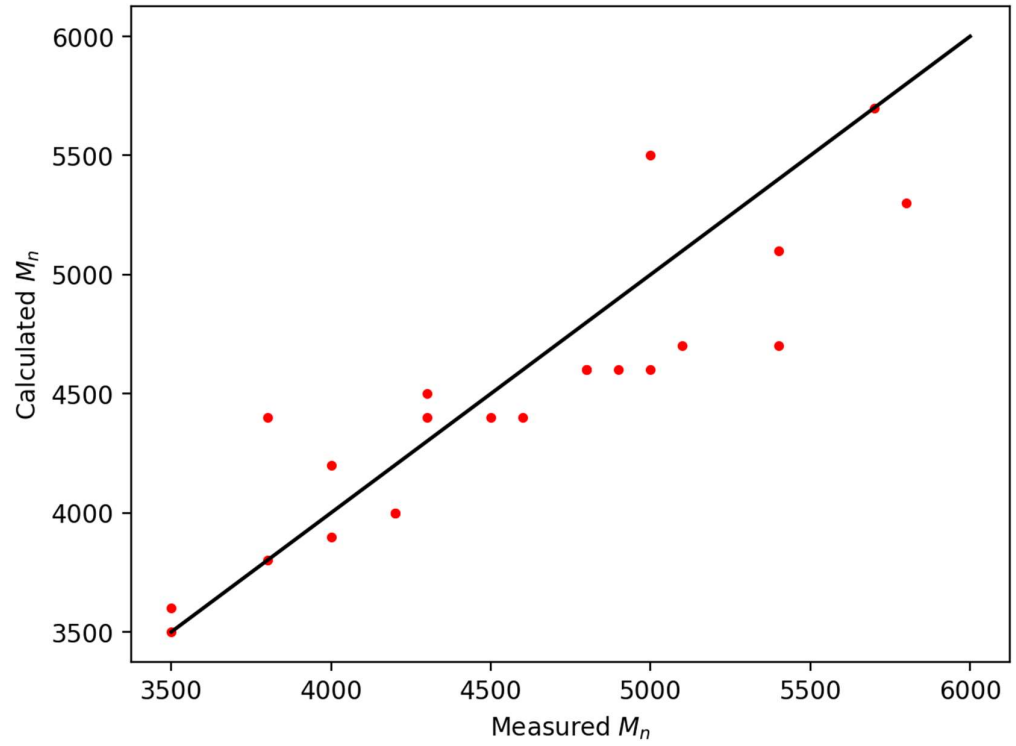


Figure 4-17 Parity of plot M_n.

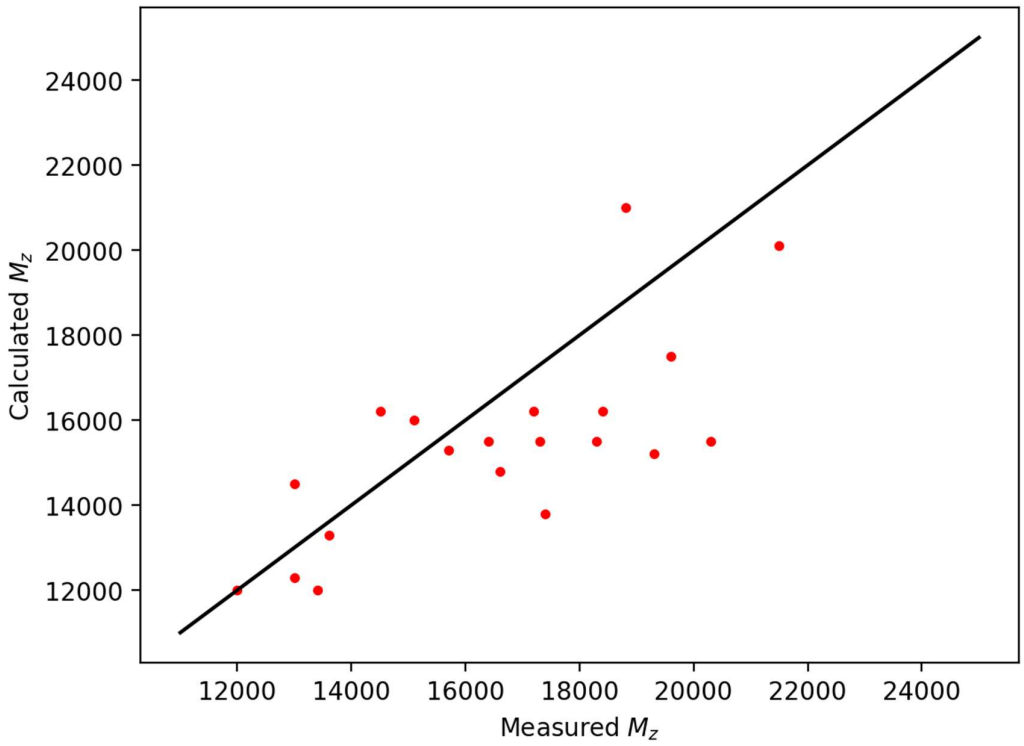


Figure 4-18 Parity plot of M_z.

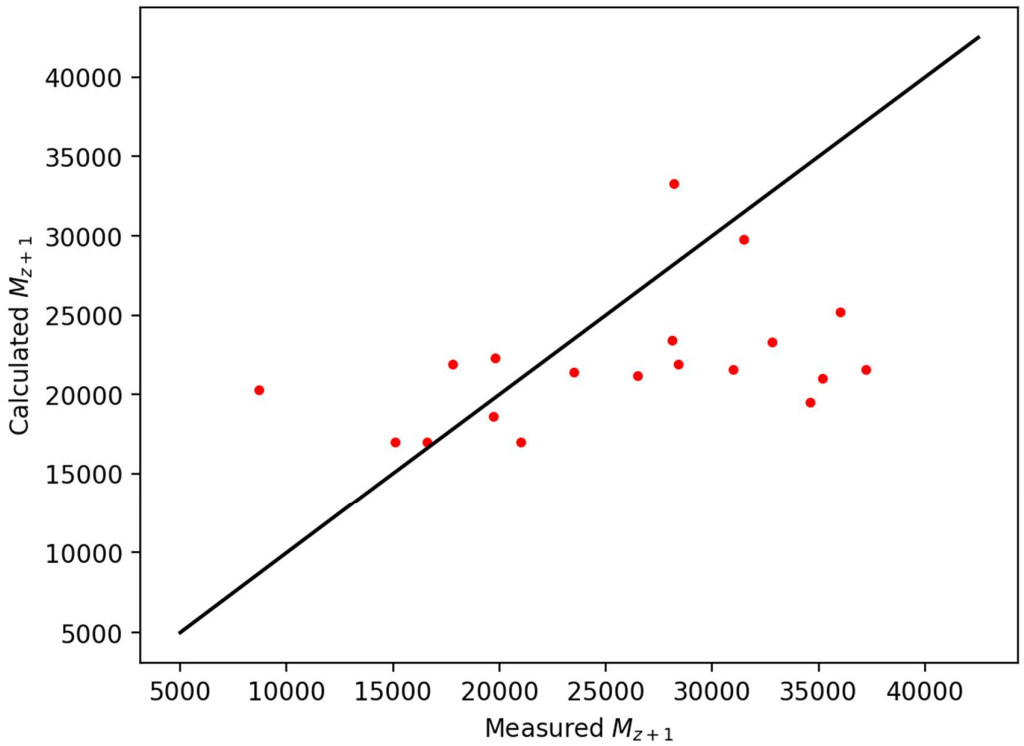


Figure 4-19 Parity plot of M_{z+1}.

4.2.6 Performance on the Validation runs

Overlay plots of measured and predicted MWD for the validation runs using the dovetail process are shown in Figure 4-20. The predicted profiles agree well with the measured MWD. Table 4-9 shows the measured molar mass averages M_w, M_n, M_z, and M_{z+1} and the ones calculated from the predicted MWD.

Table 4-9 Molar mass averages prediction on validation runs.

Run#	M_w^{exp}	M_n^{exp}	$Đ^{exp}$	M_z^E	M_{z+1}^{exp}	M_w^{pred}	M_n^{pred}	$Đ^{pred}$	M_z^{pred}	M_{z+1}^{pred}	R^2
V1	9000	4300	2.07	15800	26400	8400	4100	2.05	14100	20400	0.995
V2	10800	4800	2.27	21600	46600	9900	4700	2.10	16400	23500	0.996
V3	11000	4800	2.27	22400	50100	10400	4900	2.11	17300	25000	0.999
V4	10300	4500	2.26	21700	49500	9800	4600	2.11	16200	23000	0.999

A unique feature of the molar mass averages calculated from the predicted profiles is that they underpredict M_w, M_z, and M_{z+1} (Table 4-9). This can be attributed to the consistent underprediction in the high molecular weight tail, as shown in Figure 4-11.

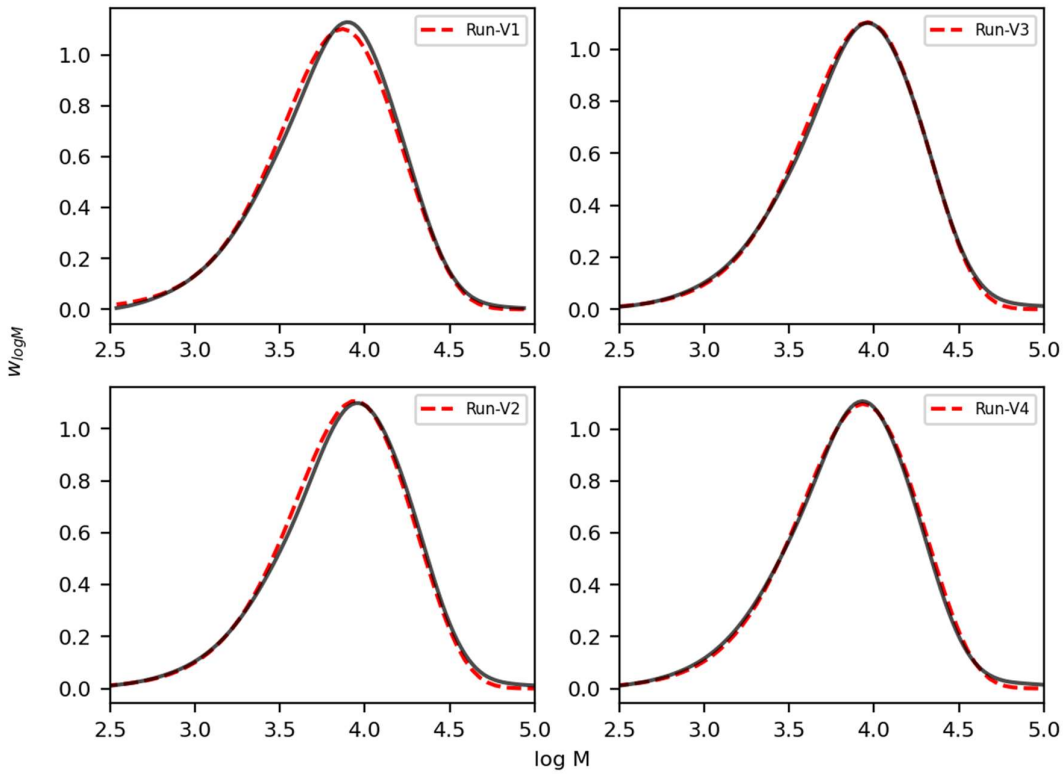


Figure 4-20 Overlay plots of validation runs.

4.2.7 Short chain branching modeling

Short chain branches (SCB) are the branches on the polyethylene backbone formed due to incorporation of 1-olefin comonomers (1-hexene, in this case) by copolymerization. The level of SCB is commonly reported as number of short chain branches per 1000 total carbon atoms.

The total CH_3 measured needs to be corrected with the chain end CH_3 groups to calculate SCB. For low molecular weight polymers, the contribution of chain end CH_3 groups increases rapidly, as shown in Figure 4-21. The expression to calculate CH_3 chain end correction for polyethylene chains of molecular weight M with no vinyl end groups is: [40]

$$N_E = \frac{28000}{M} \tag{4.22}$$

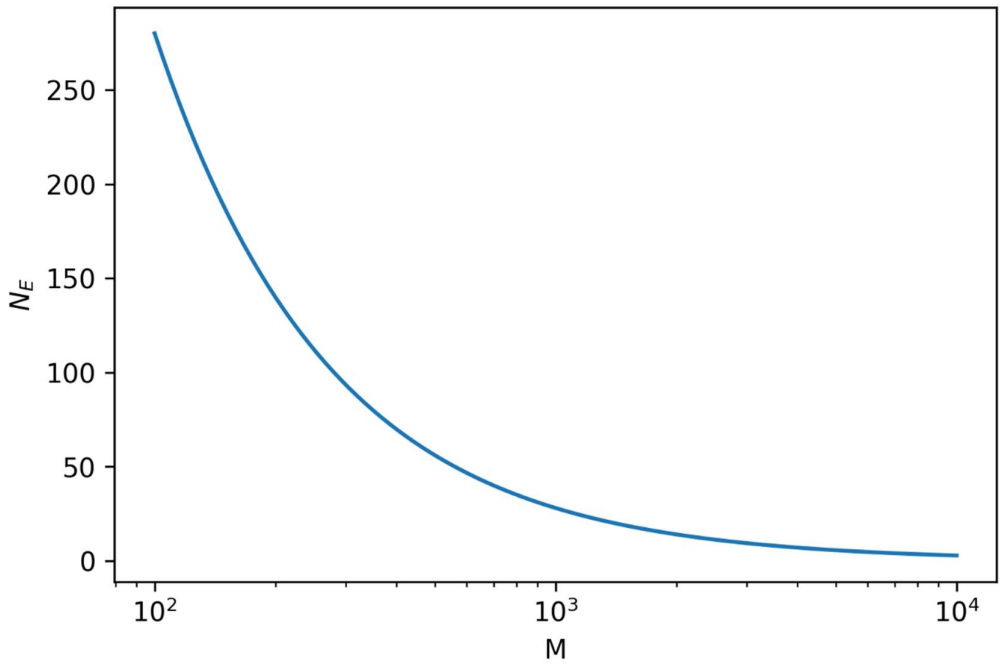


Figure 4-21 Chain end correction as a function of molecular weight.

DesLauriers and co-workers[24] reported low SCB incorporation (0-8 SCB/1000 TC) for Me_2Cp_2Si-Zr under similar reaction conditions to that used in this project. The molecular weights of DoE samples (Runs 1-22) were low ($7500 \leq M_w \leq 12100$). For such a combination of low molar mass and low SCB content, deducting N_E from total CH_3 results in large error

sometimes leading to negative values.[41] For a sample with low SCB content the main source of SCB error is attributed to a poor CH_3 signal to noise ratio. [41] The intensity of CH_3 signal is strongest at the peak of the MWD (shown for a typical sample Run 10). Hence, the SCB reported in the Table 4-10 was calculated by correcting the total CH_3 for chain ends at peak of the MWD.

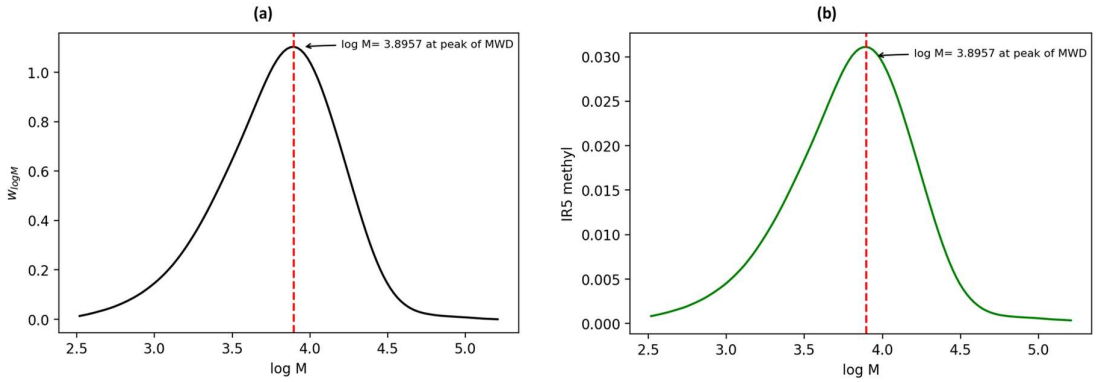


Figure 4-22 Run 10: a) MWD, b) CH_3 signal.

The SCB was modeled using the RSM approach described above for M_w and MWD. The final model was simple function of the 1-hexene/ethylene ratio,

$$SCB = 5.5386\, R \tag{4.23}$$

The parity plot is shown in Figure 4-26. Table 4-10 to 4-12 summarize the other results for this model. At SCB>4.5/1000 TC (for Runs 5,8 and 10), the SCB is underpredicted. The maximum value of R used in DoE runs was 0.8, and from Equation (4.23) the maximum SCB predicted was 4.43 SCB /1000TC. The measured values for runs 5,8, and 10 were 7.08, 5.44,4.57 SCB /1000TC respectively. This explains the underprediction of runs 5,8, and 10. The predicted R^2 for SCB was 0.64.

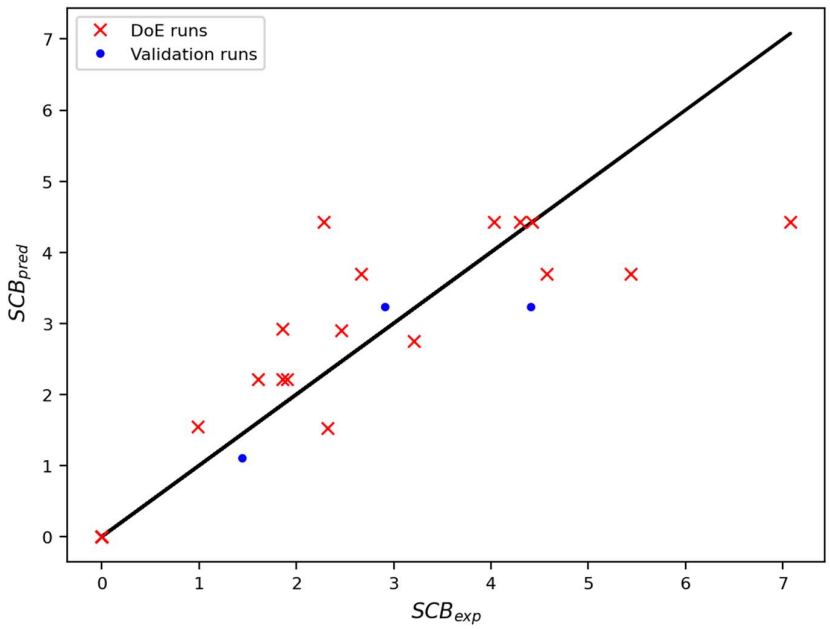


Figure 4-23 Parity plot of SCB.

Table 4-10 Measured and predicted SCB for DoE and validation runs.

Run#	SCB^{exp}	SCB^{pred}
1	1.90	2.22
2	2.46	2.90
3	0.99	1.55
4	0.00	0.00
5	7.08	4.43
6	3.21	2.75
7	1.60	2.22
8	5.44	3.70
9	4.42	4.43
10	4.57	3.70
11	2.32	1.53
12	0.00	0.00
13	2.67	3.70
14	0.00	0.00
15	0.00	0.00
16	-0.77*	N.A
17	4.03	4.43
18	0.00	0.00
19	1.85	2.22
20	2.28	4.43
21	4.29	4.43
22	1.86	2.92

V1	4.41	3.23
V2	2.91	3.23
V3	1.44	1.11
V4	-1.21*	1.11

*: SCB calculated for the Run-16 and Run-V4 were negative
N.A: not available: this data point was not included to model SCB

Table 4-11 Regression table for SCB RSM model.

SCB	Coef.	St. Error	t	p-value	95 % CI
R	5.5386	0.407	13.6	***	(4.690,6.387)
R^2	0.90	**F-value**	185.5	**df (model)**	1
R^2_{adj}	0.89	**p-value**	***	**df (residuals)**	19

*** p < 0.01, ** p < 0.05, * p < 0.1

Table 4-12 ANOVA table for SCB RSM model.

Source	Sum of squares	df	F-value	p-value	Significance
Model	183.2	1	185.5	<0.001	Significant
R	59.5	1	57.4	<0.001	Significant
Residual	19.7	19	-	-	
Lack of fit	13.23	13	0.9	0.61	Not significant*
Pure error	6.52	6	-	-	-

df: degrees of freedom
level of significance α = 0.01

4.2.8 DSC Modeling

DSC analyses were performed on all the DoE runs and validation runs. The results for melting peak temperature, T_m, are shown in Table 4-13. The regression table, ANOVA table and parity plot of results of modeling the peak temperature is shown in Table 4-14, Table 4-15 and Figure 4-24. The predicted R^2 for peak temperature was 0.65. Tight scatter around the parity line on both sides (shown in Figure 4-24) indicated randomness of errors.

Table 4-13 DSC analyses results for DoE and validation runs.

Run #	T_m (°C)
1	125.19
2	125.47
3	127.82
4	134.21
5	123.31
6	123.21
7	125.67
8	121.75
9	122.10
10	124.57
11	126.74
12	129.99
13	124.38
14	131.67
15	131.06
16	126.40
17	124.22
18	132.56
19	126.11
20	120.16
21	121.36
22	126.33
V1	124.18
V2	126.05
V3	128.55
V4	129.60

Table 4-14 Regression table for T_m RSM model.

T_m	Coef.	St. Error	t	p-value	95 % CI
R	-11.560	0.881	-13.1	***	(-13.404,-9.716)
T^2	4.64×10^{-4}	1.364×10^{-4}	3.3	***	(1.67×10^{-4}, 7.60×10^{-4})
Constant	124.419	2.115	58.9	***	(119.992, 128.845)
R^2	0.91	**F-value**	93.4	**df (model)**	2
R^2_{adj}	0.90	**p-value**	***	**df (residuals)**	19

*** $p < 0.01$, ** $p < 0.05$, * $p < 0.1$

Table 4-15 ANOVA table for T_m RSM model.

Source	Sum of squares	df	F-value	p-value	Significance
Model	273	2	93.4	<0.001	Significant
R	251.6	1	172.1	<0.001	Significant
T^2	15.6	1	10.7	<0.001	Significant
Residual	27.8	19	-	-	-
Lack of fit	23.4	13	2.45	0.14	Not significant*
Pure error	4.4	6	-	-	-

df: degrees of freedom
level of significance α = 0.01

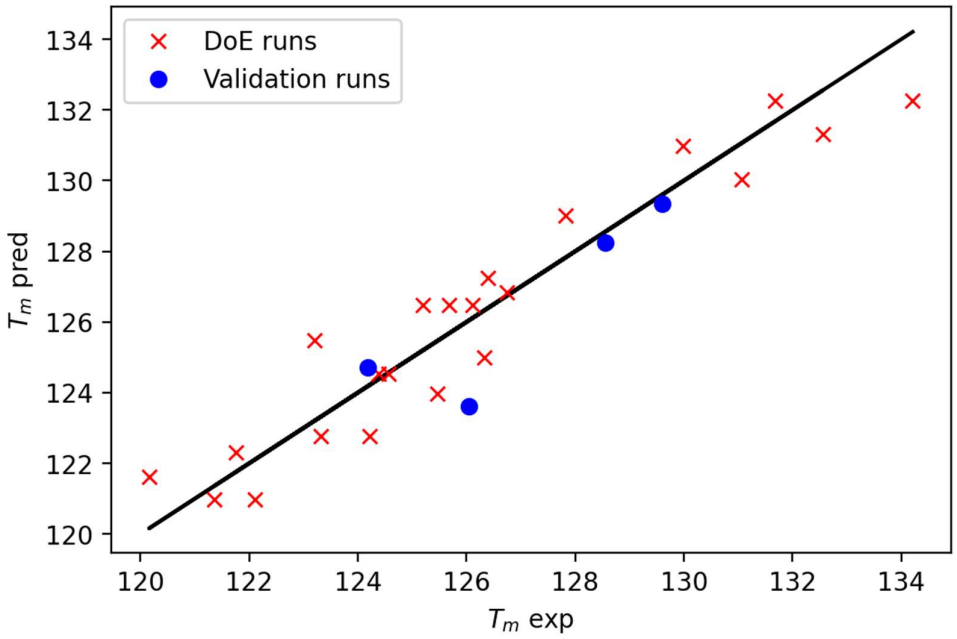


Figure 4-24 Parity plot of peak temperatures.

4.3 Explanatory Validation

Exploratory validation tests the models by predicting with them under various scenarios to assess the directional changes in prediction of the model. This exercise is performed to confirm if the model agrees with results in scientific literature. The MWD predictions were tested by changing temperature, 1-hexene/ethylene ratio, and ethylene concentration. Explanatory validation was done by: a) Compartmentalizing the log M space into low, middle, and high M

regions and visualizing what happens when input factors are changed in a controlled manner, b) Predicting the MWD by changing one input factor at a time.

4.3.1 Low, Middle, and High Molecular Weight Regions

Distributions are harder to be visualized when changing multiple input factors. Hence the log M space was segregated into three regions as low, middle, and high M regions. The boundaries of these regions are shown in Figure 4-25.

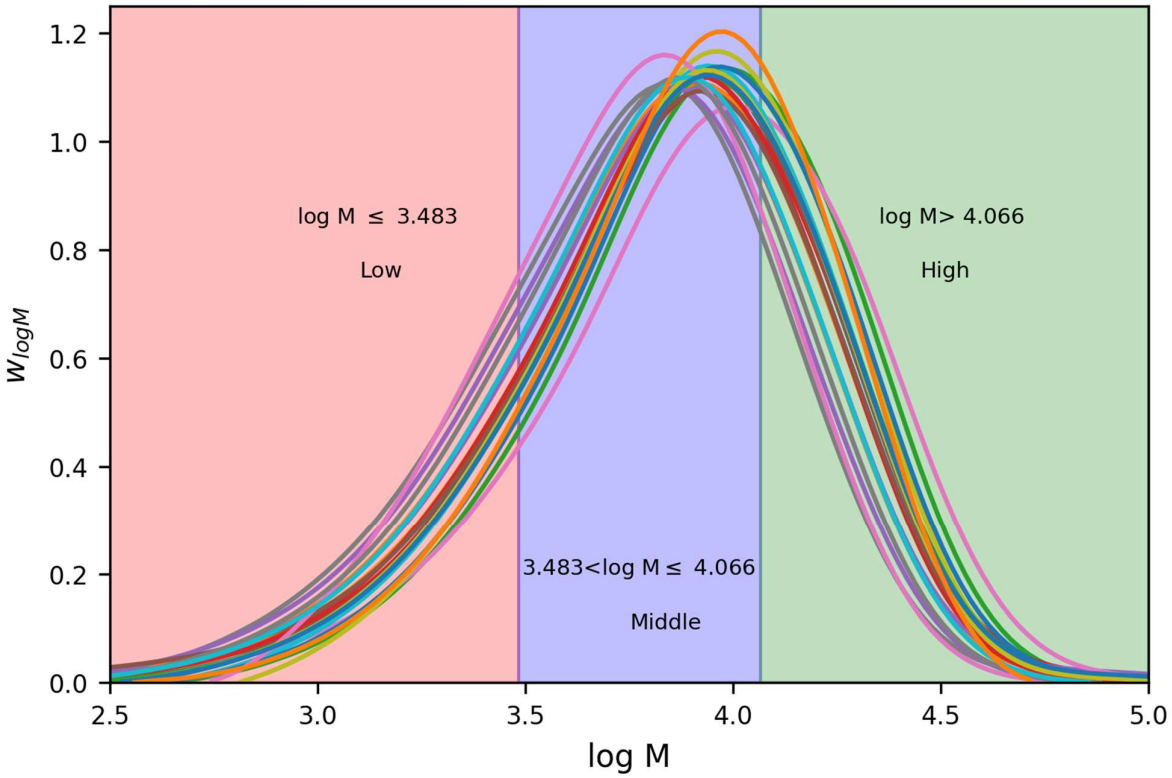


Figure 4-25 Low, middle, and high M regions.

The low, middle, and high mass fractions for the DoE runs and the MWD predictions are calculated and plotted as shown in Figure 4-26. Tight scatter around parity line for low and high M regions showed that these regions are well predicted. Wider scatter around the parity line for the mid MW region was expected as some of the models in this region were unacceptable. The mass fractions of sample in each of the regions is obtained by integrating the MWD between appropriate limits as shown in Equations (4.24) - (4.26).

$$m_{low} = \int^{3.483} w(\log M)\, \mathrm{d}(\log M) \tag{4.24}$$

$$m_{middle} = \int_{3.483}^{4.066} w(\log M)\, \mathrm{d}(\log M) \tag{4.25}$$

$$m_{high} = \int_{4.066} w(\log M)\, \mathrm{d}(\log M) \tag{4.26}$$

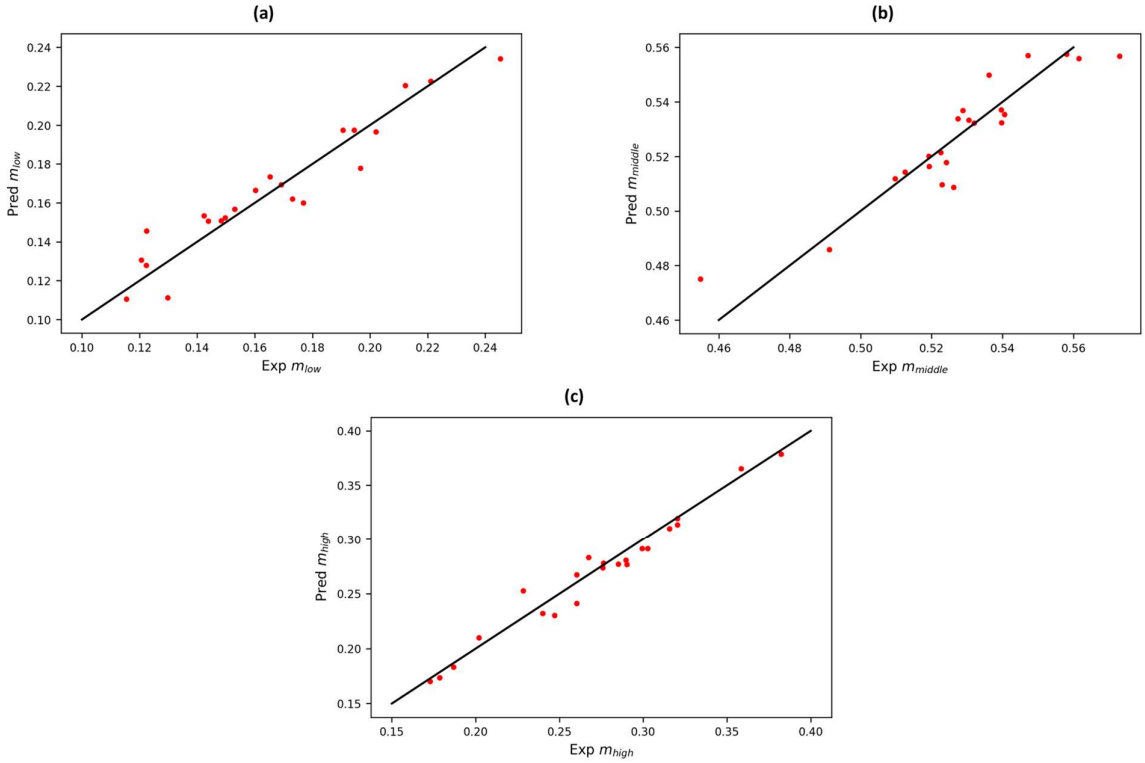


Figure 4-26 Parity plots of a) low M region, b) middle M region, c) high M regions.

Figure 4-27 shows that the mass fractions in the low and the middle *M* regions increase and the mass fraction in the high *M* region decreases as the ethylene concentration decreases and 1-hexene/ethylene ratio increases. This can be explained by the shift of MWD towards lower molecular weights as the rate of propagation decreases. Figure 4-28 shows that the mass fractions in the low and the middle *M* regions increases and the mass fraction in the high *M* region decreases as the ethylene concentration decreases and temperature increases. When

ethylene concentration decreases (decreasing propagation rate) and the temperature increases (increasing termination-to-propagation ratio) the MWD moves towards lower molecular weights. Figure 4-29 shows that mass fractions in the low and the middle *M* regions increases and the mass fraction in the high *M* region decreases, as the 1-hexene/ethylene ratio and temperature increases. When temperature increases (increasing termination rate) and the 1-hexene/ethylene ratio increases (decreasing propagation rate) the MWD moves towards lower molecular weights.

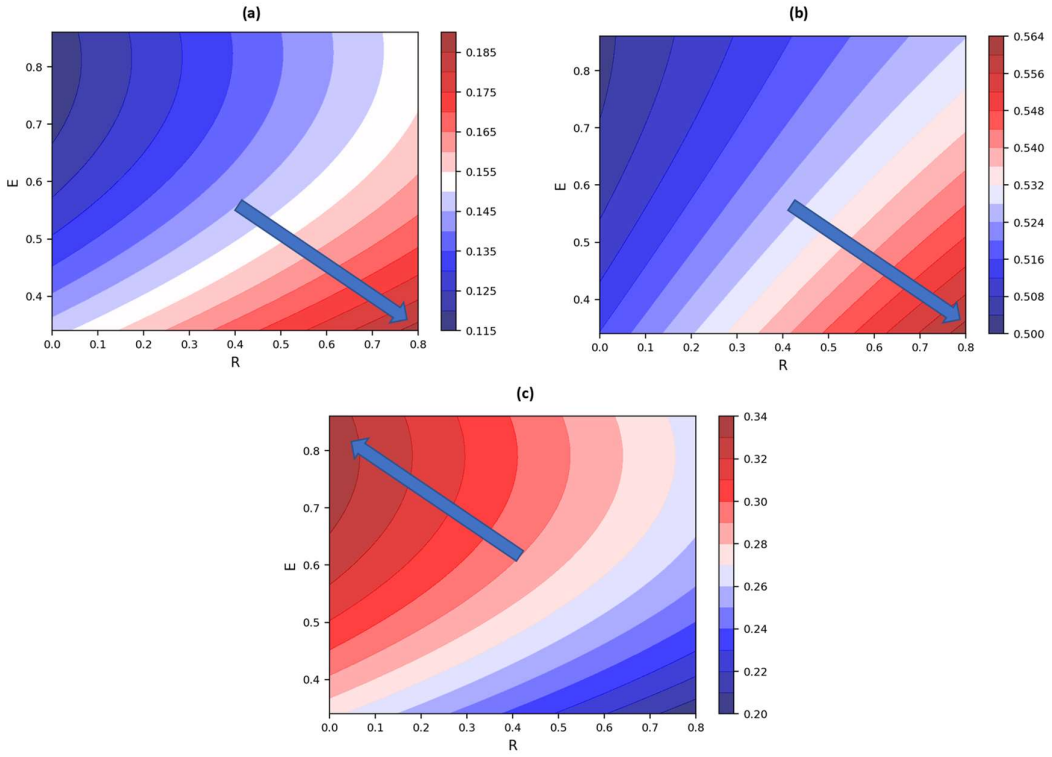


Figure 4-27 E × R at T = 120 ^{0}C contour plot: a) low, b) middle, c) high *M* regions.

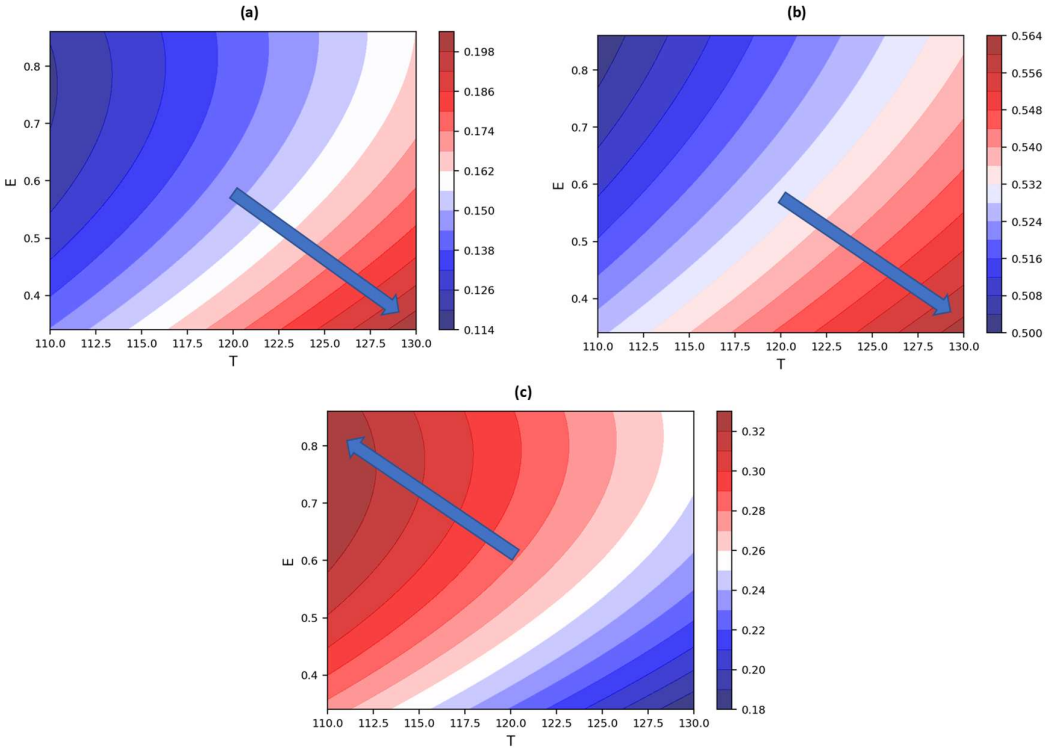


Figure 4-28 E × T at R=0.5 contour plot: a) low, b) middle, c) high *M* regions.

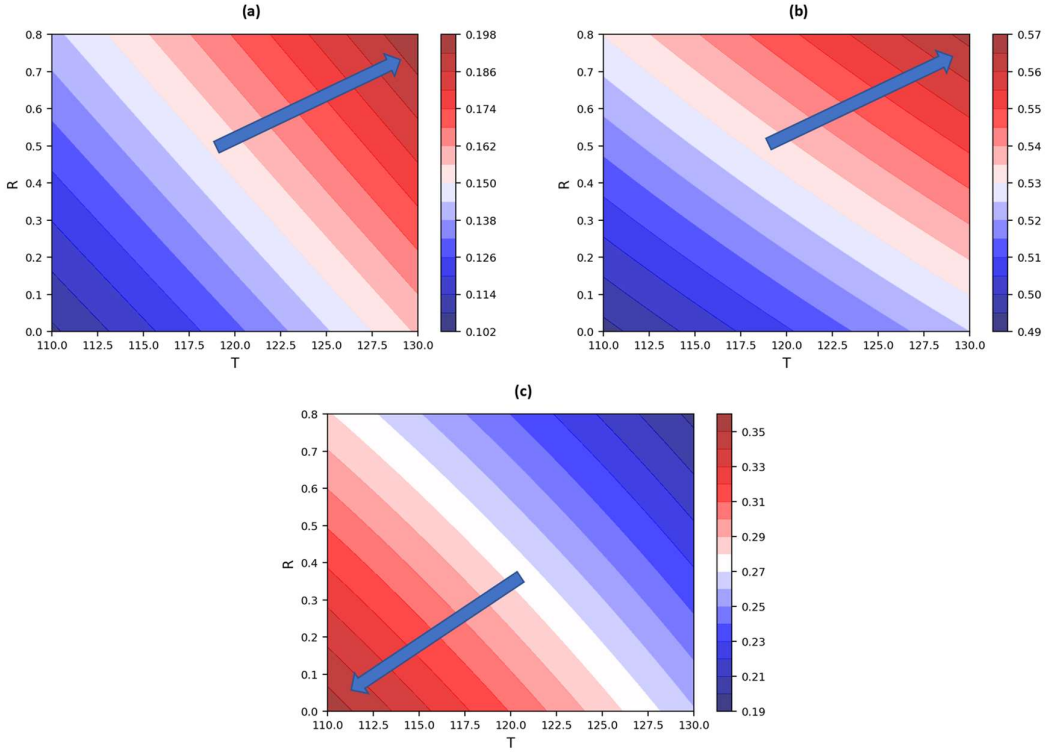


Figure 4-29 R × T at E= 0.5 mol/L contour plot a) low, b) middle, c) high *M* regions.

4.3.2 Effect of Temperature, Ethylene Concentration, and Ratio

As temperature increases at constant 1-hexene/ethylene ratio and ethylene concentration ($R = 0.5$, $E = 0.5$ mol/L), the termination rate increases and hence the MWD shifts towards lower molecular weights (Figure 4-30).

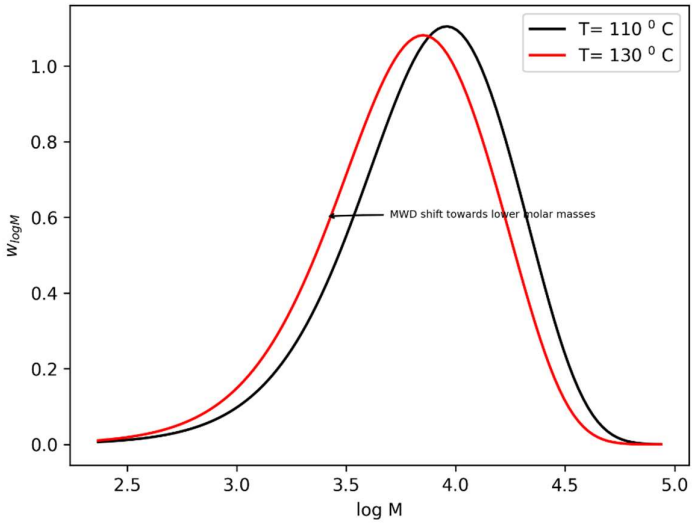


Figure 4-30 Effect of temperature on predicted MWD.

As 1-hexene/ethylene ratio increases at constant ethylene concentration and temperature ($E = 0.5$ mol/L, $T = 120$ ^{0}C), the propagation rate decreases and the MWD shifts towards lower molecular weights (Figure 4-31).

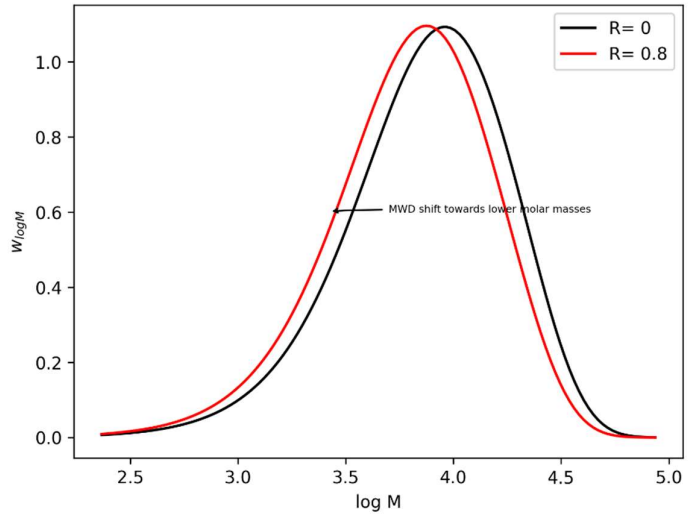


Figure 4-31 Effect of 1-hexene/ethylene ratio on predicted MWD.

As ethylene concentration increases at constant 1-hexene/ethylene ratio and temperature ($R = 0.5$, $T = 120\,^{0}$C), the propagation rate increases and the MWD shifts towards higher molecular weights (Figure 4-32).

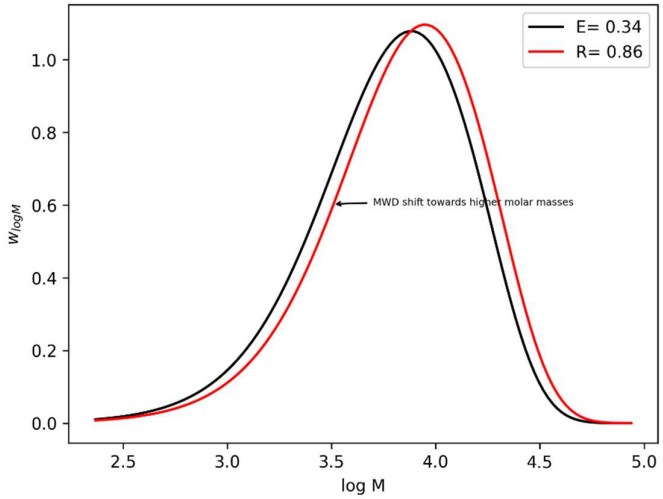


Figure 4-32 Effect of ethylene concentration on predicted MWD.

4.4 Connect Between Theoretical and Empirical RSM Modeling Approach

Empirical modelling is a type of modeling approach where models of different kinds predict responses of interest by applying techniques that are often not explainable by first principles. Empirical modeling usually results in models that predict the response well but do not offer any insight of the physics or the mechanism in the system. This modeling however useful, could also result in models that are not generalizable. Hence caution needs to be exercised by the modeler when building and using these models.

A connection between the empirical approach and the first principles generates confidence in potential users and makes a credible case for deployment of these methods. The empirical modeling approach applied in this work is the response surface modeling. Response surface methods use simple polynomial type equations to model response within experimental space. A philosophical argument is made here to bridge the two approaches: empirical and first principles. In Section 4.2.1, we showed that molecular weight average $M_w$was modeled adequately by a RSM model.

Combining Equations (4.3) and (4.7), for single site polyethylenes we have:

$$M_w = \frac{2}{\hat{\tau}} \tag{4.27}$$

From Equation (4.28), we can conclude that $\hat{\tau}$ and by extension τ can be modeled by a RSM model (let us call them $F_2(E,R,T)$ and $F_1(E,R,T)$ respectively). Let us take a specific example of single site polyethylenes with the kinetics mechanisms as shown in Table 2-9. The rate constants in the $\widetilde{k_{tH}}$, $\widetilde{k_{tM}}$, $\widetilde{k_{t\beta}}$, $\widetilde{k_{tAl}}$, and $\widetilde{k_p}$ can be expressed through a simple generic form of the Arrhenius law as (shown for the case of $\widetilde{k_p}$):

$$\widetilde{k_p} = \widetilde{k_{p_0}} exp\left(\frac{-E_{\widetilde{k_p}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \tag{4.28}$$

where, T_0 is a reference temperature, $\widetilde{k_{p_0}}$ is the pseudo propagation rate constant at reference temperature, $E_{\widetilde{k_p}}$ is the activation energy associated with the pseudo propagation rate constant. In Equations (2.10)-(2.28), let us consider ethylene as monomer A and 1-hexene as monomer B. When all the terms with their expansions of all the rate constants are put together in Equation (2.30) to express τ, it results in a complex function of ethylene concertation, 1-hexene concentration, and temperature. The 1-hexene concentration can be divided by the ethylene concentration to get the 1-hexene/ethylene ratio. The RSM models $F_1(E,R,T)$ and $F_2(E,R,T)$ for τ and $\hat{\tau}$ approximated the complex relationship of these factors derived from first principles.

Let us consider the case of predicting the MWD by discretizing the $\log M$ space. The height of the MWD in each $\log M$ slice can be expressed by Flory's distribution and is shown in Equation (2.31) which is repeated here for the sake of illustration:

$$w(\log M) = 2.3026\, M^2\, \hat{\tau}^2 \exp(-M\hat{\tau}) \tag{4.29}$$

Taylor series expansion for exponential function is shown in Equation (4.30):

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \tag{4.30}$$

The exponential term in Equation (4.29) can be expanded by applying Taylor series expansion and the resultant expression is:

$$w(\log M) = 2.3026\, M^2\, \hat{\tau}^2 \left(1 - M\hat{\tau} + \frac{(M\hat{\tau})^2}{2!} - \frac{(M\hat{\tau})^3}{3!} + \ldots.\right) \tag{4.31}$$

The term in the bracket in Equation (4.31) can be usually approximated by truncating it to a few terms based on the importance of terms. Since $\hat{\tau} = F_2(E, R, T)$, the term in the bracket can be represented by another function of *"E", "R",* and *"T"* (let us call it $F_3(E, R, T)$).

$$w(log\ M) = 2.3026\, M^2 F_2^2\ (E, R, T)\ (F_3(E, R, T)) \tag{4.32}$$

$$w(log\ M) = M^2 F_4(E, R, T) \tag{4.33}$$

In conclusion, the RSM models for $\log M$ slices truncate the expansion and encapsulate the relationship in a simple polynomial form and provides an approximation. As we have seen in Sections 4.2.5 and 4.2.6, the dovetail process comprising of RSM modeling and tail approximation modeled and predicted the MWD adequately. Response surface methods and artificial neural networks have been successfully deployed to estimate polymerization kinetic rate constants, [42] optimize for copolymer microstructure, [43] and model MFI, crystallinity, yield, and polymerization activity. [44]

4.5 Targeted Resin Design Using RSM models

The overarching goal of developing tools to simulate microstructure is to save time and material when designing new resins. The dovetail process provides a simplified mathematical approach to link reactor conditions (temperature, 1-hexene/ethylene ratio, and ethylene concentration) to MWD, SCB, and T_m. One can then reverse the flow and estimate the reaction conditions required to synthesize resins withs desired microstructure. A schematic of the forward and reverse processes is shown in Figure 4-33.

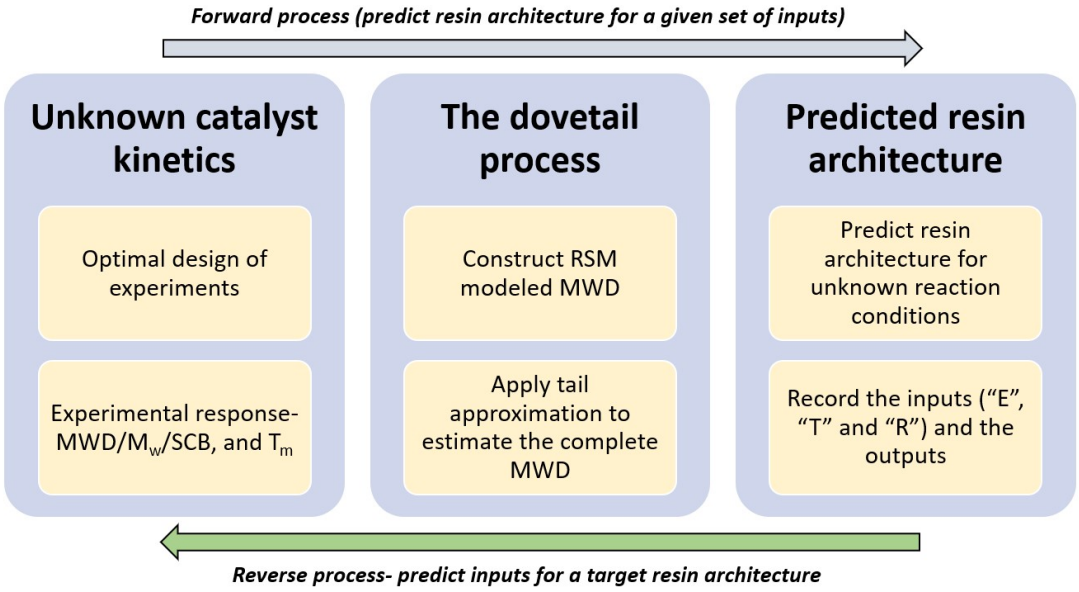


Figure 4-33 Forward and reverse processes.

An objective function (Equation (4.34)) was formulated by taking squared sum of error from MWD and SCB. The objective function has contributions from error in MWD and SCB. They are weighed based on their importance which can be adjusted based on the intended goal.

$$\textbf{minimize} \quad F(x) = \sum_{i=1}^{n} a\,(MWD_{t,i} - MWD_{x,i})^2 + b\,(SCB_t - SCB_x)^2 \qquad (4.34)$$

The terms in Equation (4.34) are:

- $MWD_{t,i}$ is the height of the MWD at the log M point numbered i in the target MWD.
- $MWD_{x,i}$ is the height of the MWD (predicted at input conditions (x)) at the log M point numbered i.
- a is the weight attributed to MWD.
- b is the weight attributed to SCB.
- SCB_t is the SCB of target resin.
- SCB_x is the SCB predicted for the input conditions (x).
- x is the input factor vector to needs to be found that minimizes $F(x)$. The input factor vector is 1 x 3 row vector in the format [E, T, R]

The objective function (Equation (4.34)) was subjected to bounds in input factors shown in Equations (4.35)-(4.37). The bounds for the input vector came from the bounds of the factors

in the DoE. The parameters a and b chosen were 0.98 and 0.02 respectively. The reason why a higher value of a was chosen was those errors in MWD are one order magnitude smaller compared to errors in SCB. Hence if they are equal, the optimizer would return a solution that would try to fit the SCB better at the expense of poorly fitting the MWD. The DoE runs were used as targets to perform the reverse process and the results are presented in Table 4-16. The SLSQP minimization algorithm as implemented in the module "*scipy.optimize.minimize*" on Python 3 was used for the minimization. [45] The initial guesses were randomly generated in the input factor space. As noted in Section 4.2.7 the SCB calculated for Run-16 was negative. The SCB was set to 1.33, calculated based on the RSM model developed in the Section 4.2.7 so that the reverse process could be performed on it.

$$x[1] \geq 0.34 \qquad x[1] \leq 0.86 \tag{4.35}$$

$$x[2] \geq 110 \qquad x[2] \leq 130 \tag{4.36}$$

$$x[3] \geq 0 \qquad x[3] \leq 0.8 \tag{4.37}$$

$$a + b = 1 \tag{4.38}$$

Table 4-16 Reaction conditions calculated by the reverse process.

Run#	E^{exp}	T^{exp}	R^{exp}	E^{pred}	T^{pred}	R^{pred}	$F(x)$
Run-1	0.6	120	0.4	0.38	111	0.438	0.037
Run-10	0.84	130	0.668	0.77	126	0.787	0.029
Run-11	0.86	110	0.276	0.73	112	0.313	0.0273
Run-12	0.35	119	0	0.57	125	0.037	0.026
Run-13	0.84	130	0.668	0.61	128	0.486	0.036
Run-14	0.64	130	0	0.60	126	0.054	0.025
Run-15	0.55	110	0	0.68	113	0	0.093
Run-17	0.41	128	0.8	0.34	124	0.8	0.05
Run-18	0.85	122	0	0.82	116	0.249	0.121
Run-19	0.6	120	0.4	0.42	111	0.402	0.038
Run-2	0.63	110	0.524	0.78	114	0.422	0.017

Run-20	0.54	118	0.8	0.50	120	0.423	0.023
Run-21	0.81	112	0.8	0.77	118	0.6	0.042
Run-22	0.86	120	0.528	0.79	127	0.355	0.019
Run-3	0.34	130	0.28	0.34	130	0.271	0.043
Run-4	0.64	130	0	0.53	127	0.032	0.043
Run-5	0.41	128	0.8	0.46	130	0.8	0.21
Run-6	0.34	121	0.496	0.36	122	0.609	0.021
Run-7	0.6	120	0.4	0.43	114	0.346	0.029
Run-8	0.35	110	0.668	0.40	115	0.8	0.035
Run-9	0.81	112	0.8	0.69	113	0.734	0.021
Run-16	0.35	110	0.24	0.45	111	0.271	0.166

As can be seen from Table 4-16, the solutions for ethylene concentration, temperature, and comonomer ratio found are different from DoE reaction conditions. The solution from the reverse process depends on the initial guess and multiple solutions are possible. Hence, this reverse process for all the runs were run 10 times to obtain solution sets (for all the 22 DoE runs). For each run, the solution that corresponded to the minimum value of objective function ($F(x)$) among all the 10 solutions were chosen as the final solution and the results are shown in Table 4-17. These solutions will be called the "best solution".

Table 4-17 Best solutions reaction conditions.

Run#	E^{exp}	T^{exp}	R^{exp}	E^{pred}	T^{pred}	R^{pred}	$F(x)$
Run-1	0.6	120	0.4	0.79	125	0.317	0.0202
Run-10	0.84	130	0.668	0.49	119	0.800	0.0257
Run-11	0.86	110	0.276	0.73	112	0.313	0.0273
Run-12	0.35	119	0	0.59	126	0.032	0.0257
Run-13	0.84	130	0.668	0.61	128	0.488	0.0361
Run-14	0.64	130	0	0.72	128	0.042	0.0186
Run-15	0.55	110	0	0.68	113	0	0.0930
Run-17	0.41	128	0.8	0.41	130	0.715	0.0327
Run-18	0.85	122	0	0.86	123	0.008	0.0417
Run-19	0.6	120	0.4	0.81	122	0.293	0.0225
Run-2	0.63	110	0.524	0.63	111	0.465	0.0152
Run-20	0.54	118	0.8	0.75	126	0.409	0.0225
Run-21	0.81	112	0.8	0.68	112	0.735	0.0148
Run-22	0.86	120	0.528	0.79	127	0.355	0.0192
Run-3	0.34	130	0.28	0.34	130	0.272	0.0429
Run-4	0.64	130	0	0.53	127	0.032	0.0432
Run-5	0.41	128	0.8	0.37	125	0.800	0.2034
Run-6	0.34	121	0.496	0.41	124	0.602	0.0203
Run-7	0.6	120	0.4	0.82	124	0.274	0.0151

Run-8	0.35	110	0.668	0.44	117	0.800	0.0337
Run-9	0.81	112	0.8	0.61	110	0.800	0.0182
Run-16	0.35	110	0.24	0.86	120	0.22	0.096

The overlay plots using the best solution are shown in Figure 4-34. The MWDs predicted by the best solutions matched the experimentally measured MWDs. The parity plot of SCB calculated from the best solution is shown in Figure 4-35. Measured SCB are plotted on x-axis and SCB predicted from the "best solutions" are plotted in Figure 4-35. A tight scatter around the parity line with two outliers from runs 5 and 8 was observed. The upper bound for 1-hexene/ethylene ratio was 0.8 (Equation (4.37)). At $R = 0.8$, the model for SCB (Equation (4.23)) predicted SCB of 4.43 SCB /1000TC. The target SCB values for runs 5 and 8 were 7.08 and 5.44. Hence, the best solution for runs 5 and 8 predict below the SCB targets.

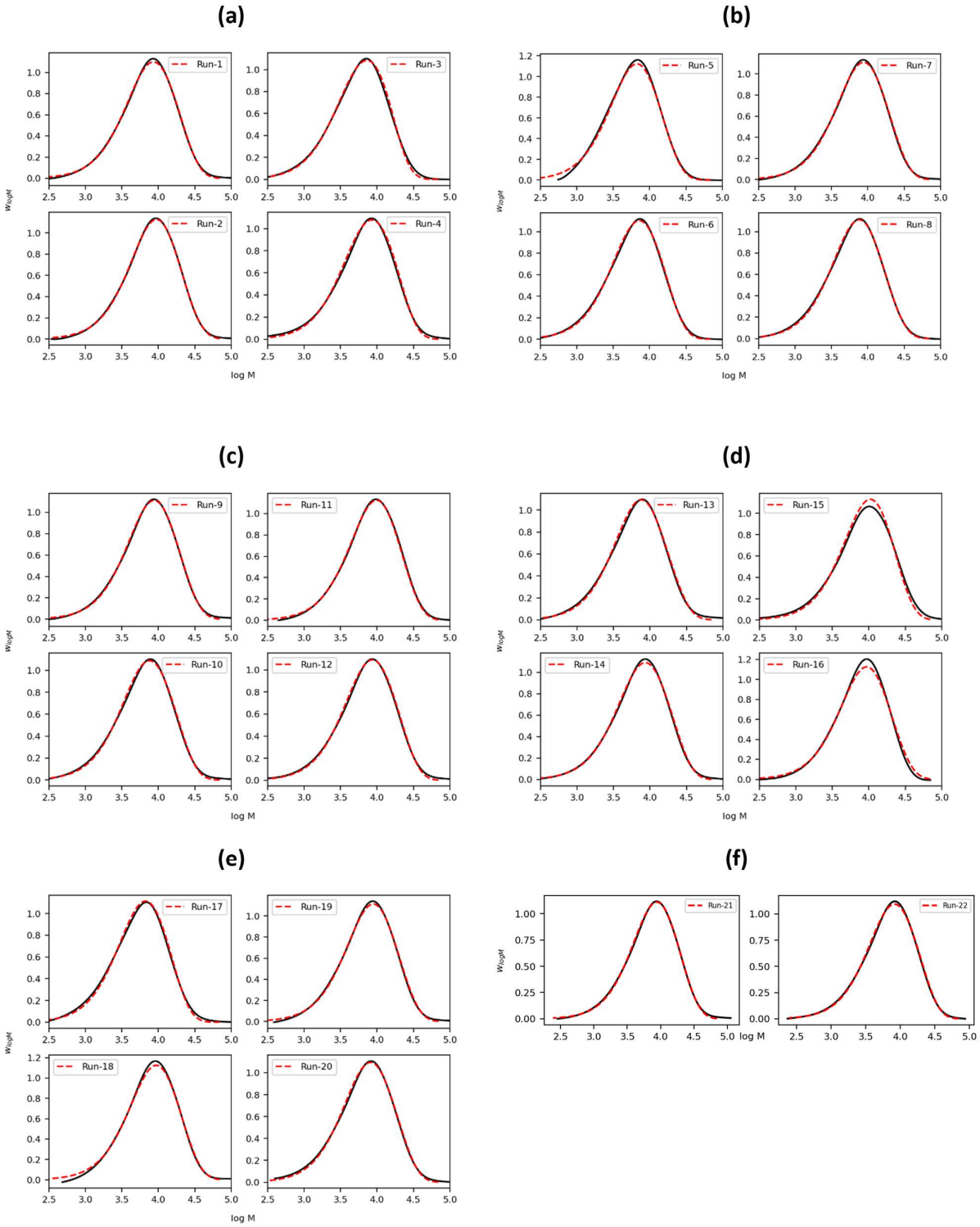


Figure 4-34 Overlay plots for best solution: a) runs 1-4, b) runs 5-8, c) runs 9-12, d) runs 13-16, e) runs-17-20, f) runs 21 and 22.

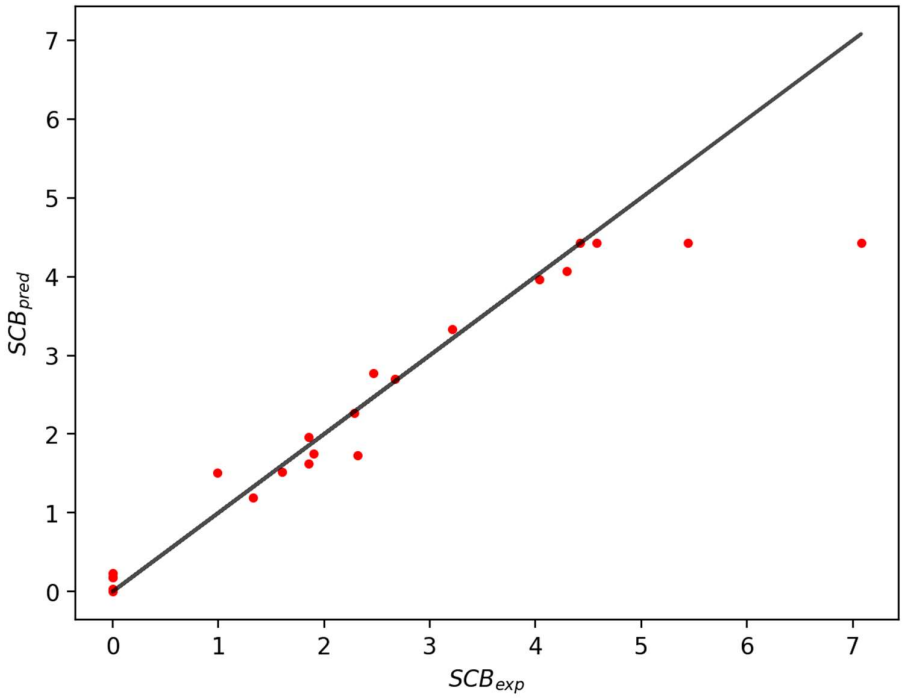


Figure 4-35 Parity plot of SCB from the best solutions.

Multiple solutions obtained by the reverse process can be differentiated based their values of E, T, and R. A simple function that penalizes E, T, and R for deviations from their minimum values (shown in Table 4-1) can be defined as:

$$p(x) = \left(\frac{x[1] - 0.34}{0.86 - 0.52}\right) \text{ x } \left(\frac{x[2] - 110}{130 - 110}\right) \text{ x } \left(\frac{x[3] - 0}{0.8 - 0}\right) \tag{4.39}$$

where, x is the solution as 1 x 3 row vector in the format [*E, T, R*]. The 10 solutions obtained to target Run-1 and their $p(x)$ values calculated by using Equation (4.39) were ranked based on their $p(x)$ values and are shown in Table 4-18. The predicted and target MWDs for Run-1 are shown in Figure 4-36.

Table 4-18 Multiple solutions for Run-1.

Solution #	E^{pred}	T^{pred}	R^{pred}	$p(x)$	SCB^{pred}
1	0.38	111	0.438	1.54 x 10^{-3}	2.43
2	0.44	115	0.393	2.38 x 10^{-2}	2.18
3	0.47	116	0.395	3.44 x 10^{-2}	2.19

4	0.53	119	0.347	7.35×10^{-2}	1.92
5	0.56	120	0.362	9.60×10^{-2}	2.01
6	0.62	121	0.390	1.41×10^{-1}	2.16
7	0.80	129	0.182	1.95×10^{-1}	1.01
8	0.82	129	0.194	2.17×10^{-1}	1.07
9	0.73	122	0.387	2.22×10^{-1}	2.14
10	0.79	125	0.317	2.58×10^{-1}	1.76

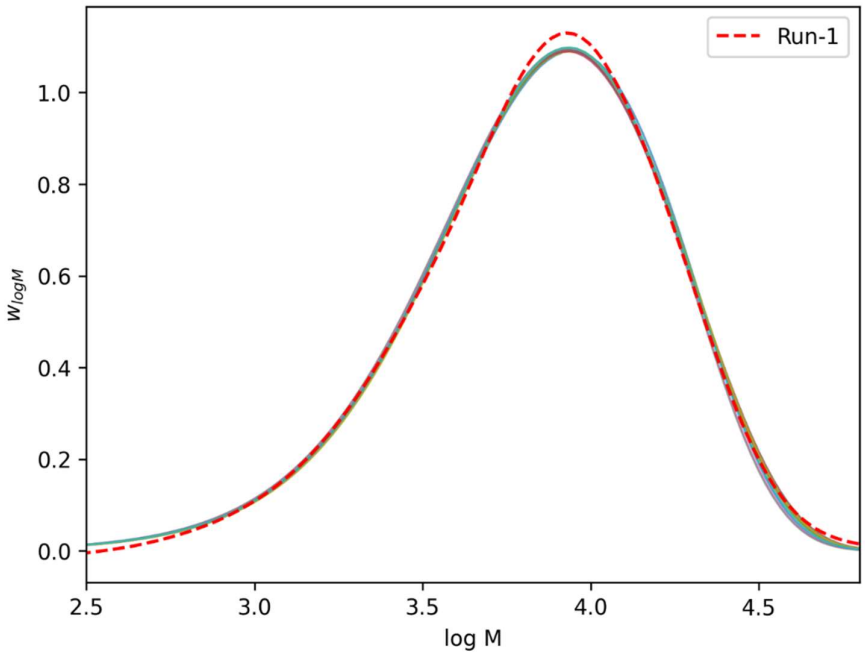


Figure 4-36 Predicted and target MWDs for Run-1.

Solution # 1: [0.38,111,0.438] (Table 4-18) has the lowest $p(x)$ value. This has the least deviation in reaction conditions from minimum values of [0.34,110,0] among all the solutions. Solution # 6: [0.62,121,0.39] (Table 4-18) is close to the reaction conditions in the DoE ([0.6,120,0.40]) for Run-1. From an economic standpoint, if reactor conditions from Solution # 1 are employed in the solution reactor, it will have the least ethylene partial pressure and 1-hexene concentration. Reaction conditions influence the operating costs of the reactor, hence defining penalty/desirability functions that incorporate economic considerations can aid in optimal choice of reaction conditions.

5. Conclusions and recommendations

In this thesis, we set out to develop a methodology to predict microstructure of ethylene/1-hexene copolymers. This was done by solution polymerization setup to illustrate essential features of a polymerization system. An integrated variance optimal design aimed to minimize the average prediction variance over the input factor space. Molar mass average M_w, SCB, and T_m were modeled, and predicted. The $\log M$ space was discretized extending an analogous idea proposed by DesLauriers et al. [24] RSM models were built for each point on the $\log M$ space. Model acceptance criteria were set to assess the statistical significance of regression and lack of fit. The process of discretization of $\log M$ space omitted the low and high M tails. To address this gap a second part to the prediction process called "tail approximation" was added. This process adequately predicted the MWD of DoE runs, and the validation runs from baseline to baseline.

The $\log M$ space was divided into three slices: low, middle, and high M regions. The effect of input factors on mass fractions of polymers in these regions were investigated and found to be reasonable. Explanatory validation was also performed by investigating the effect of input factors one at a time to confirm their validity. Furthermore, a philosophical argument was made to illustrate how the empirical RSM modeling approach approximated the fundamental kinetic models.

In conclusion, the RSM modeling approach was successfully applied to do forward predictions. More importantly, it was shown that this process could be reversed to determine reactor conditions to synthesize target polymers. The reverse process generated multiple solutions. A simple function ranked the multiple solutions. When these functions are formulated to incorporate economic considerations, they could differentiate between solutions. Further polymerization experiments could be done to synthesize them and test them for different end use properties. RSM modeling approach can be applied to reaction rates to test their ability to estimate kinetic parameters. The RSM modeling tool for microstructure developed in this thesis represents a novel simplified approach to resin design.

References

1. History and Future of Plastics | Science History Institute. https://www.sciencehistory.org/the-history-and-future-of-plastics.
2. Bakelite First Synthetic Plastic - National Historic Chemical Landmark - American Chemical Society. https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/bakelite.html.
3. Plastic - History Learning Site. https://www.historylearningsite.co.uk/inventions-and-discoveries-of-the-twentieth-century/plastic/.
4. Natural vs Synthetic Polymers - Gelfand Center - Carnegie Mellon University. https://www.cmu.edu/gelfand/lgc-educational-media/polymers/natural-synthetic-polymers/index.html.
5. Nucleic Acid. https://www.genome.gov/genetics-glossary/Nucleic-Acid.
6. Explainer: What are polymers? | Science News for Students. https://www.sciencenewsforstudents.org/article/explainer-what-are-polymers.
7. Shrivastava, A. Introduction to Plastics Engineering. in *Introduction to Plastics Engineering* 1–16 (Elsevier, 2018). doi:10.1016/b978-0-323-39500-7.00001-0.
8. Mallick, P. K. Thermoplastics and thermoplastic-matrix composites for lightweight automotive structures. in *Materials, Design and Manufacturing for Lightweight Vehicles* 174–207 (Elsevier Ltd., 2010). doi:10.1533/9781845697822.1.174.
9. Thermoset vs. Thermoplastics - A Comparison of Materials, Advantages and Disadvantages. https://www.thomasnet.com/articles/plastics-rubber/thermoset-vs-thermoplastics/.
10. Thermoset vs. Thermoplastic: Which is Right for My Product? https://news.ewmfg.com/blog/thermoset-vs.-thermoplastic-which-is-right-for-my-application.
11. Polyolefin Market Research Report -Global Forecast to 2022. https://www.marketresearchfuture.com/reports/polyolefin-market-1695.
12. Polyolefins Market Size, share, growth Analysis-2020. https://www.marketdataforecast.com/market-reports/Polyolefin-market.
13. Peacock, A. J. *HANDBOOK OF POLYETHYLENE Structure, Properties and Applications*. *Marcel Dekker, Inc.* (2000).
14. McDaniel, M. P. & DesLauriers, P. J. *Ethylene Polymers, HDPE*. *Kirk-Othmer*

Encyclopedia of Chemical Technology (2015). doi:10.1002/0471238961.0809070811091919.a01.pub3.

15. Touloupidis, V. Catalytic Olefin Polymerization Process Modeling: Multi-Scale Approach and Modeling Guidelines for Micro-Scale/Kinetic Modeling. *Macromol. React. Eng.* **8**, 508–527 (2014).
16. McKenna, T. F. & Soares, J. B. P. *Handbook of Polyolefin Reaction Engineering*. (2012).
17. Matos, V., Mattos Neto, A. G., Nele, M. & Pinto, J. C. Method for quantitative evaluation of kinetic constants in olefin polymerizations. II: Kinetic study of a high-activity Ziegler-Natta catalyst used for bulk propylene polymerizations. *J. Appl. Polym. Sci.* **86**, 3226–3245 (2002).
18. Scott, A. J. & Penlidis, A. Design of polymeric materials: Experiences and prescriptions. *Can. J. Chem. Eng.* **99**, 5–30 (2021).
19. A History of Plastics. https://www.bpf.co.uk/plastipedia/plastics_history/Default.aspx.
20. Himmelblau, D. M. & Riggs, J. B. *Basic Principles and Calculations in Chemical Engineering*. (2012).
21. Andresen, A. *et al.* Halogen-Free Soluble Ziegler Catalysts for the Polymerization of Ethylene. Control of Molecular Weight by Choice of Temperature. *Angew. Chemie Int. Ed. English* **15**, 630–632 (1976).
22. Veiga, P., Mendes, L. & Lourenço, L. A retrospective view of statistical quality control research and identification of emerging trends: a bibliometric analysis. *Qual. Quant.* **50**, 673–692 (2016).
23. Technological Progress - Our World in Data. https://ourworldindata.org/technological-progress.
24. DesLauriers, P. J., Fodor, J. S., Mehdiabadi, S., Hegde, V. & Soares, J. B. P. Mapping the Structure–Property Space of Bimodal Polyethylene Using Response Surface Methods. Part 2: Experimental Investigation of Polymer Microstructure and Yield Estimations. *Macromol. React. Eng.* **14**, 1–21 (2020).
25. Mori, Sadao ; Barth, H. G. *Size Exclusion Chromatography*. (Springer).
26. Soares, J. B. P., Abbott, R. F. & Kim, J. D. Environmental stress cracking resistance of polyethylene: The use of CRYSTAF and SEC to establish structure-property relationships. *Journal of Polymer Science, Part B: Polymer Physics* vol. 38 1267–1275 (2000).
27. Olefin Polymerization with Ziegler-Natta Catalyst - Chemistry LibreTexts.

https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_(Inorganic_Chemistry)/Catalysis/Catalyst_Examples/Olefin_Polymerization_with_Ziegler-Natta_Catalyst.

28. Monrabal, B. Crystaf: Crystallization analysis fractionation. A new approach to the composition analysis of semicrystalline polymers. *Macromol. Symp.* **110**, 81–86 (1996).
29. Huan, X. An Introduction to Optimal Experimental Design. (2019).
30. Anthony Atkinson; Alexander Donev; Randall Tobias. *Optimum Experimental Designs, with SAS*. *Oxford University Press* (2007).
31. DesLauriers, P. J., Fodor, J. S., Soares, J. B. P. & Mehdiabadi, S. Mapping the Structure–Property Space of Bimodal Polyethylenes Using Response Surface Methods. Part 1: Digital Data Investigation. *Macromol. React. Eng.* **12**, 1–14 (2018).
32. Response Surface Models. https://abaqus-docs.mit.edu/2017/English/IhrUserMap/ihr-c-Reference-RSM.htm.
33. 11.2 - Stepwise Regression | STAT 462. https://online.stat.psu.edu/stat462/node/196/.
34. Strem Chemicals, I. Zirconium (CAS Number 86050-32-0) : Strem Product Catalog. https://www.strem.com/catalog/v/40-1115/85/zirconium_86050-32-0.
35. Caldera Palacios, A. A. Polymerization Kinetics and Structure-Property Relationships of Ethylene/1-Hexene Copolymers. (University of Alberta, 2018).
36. What Is the F-test of Overall Significance in Regression Analysis? https://blog.minitab.com/en/adventures-in-statistics-2/what-is-the-f-test-of-overall-significance-in-regression-analysis.
37. Soares, J. B. P. & Hamielec, A. E. Deconvolution of chain-length distributions of linear polymers made by multiple-site-type catalysts. *Polymer (Guildf).* **36**, 2257–2263 (1995).
38. Da Silva Filho, A. A., Soares, J. B. P. & De Galland, G. B. Measurement and mathematical modeling of molecular weight and chemical composition distributions of ethylene/α-olefin copolymers synthesized with a heterogeneous Ziegler-Natta catalyst. *Macromol. Chem. Phys.* **201**, 1226–1234 (2000).
39. How to cut a dovetail joint with a wood chisel? https://www.wonkeedonkeetools.co.uk/media/wysiwyg/11WC-Wood-Chisels-David/11WC14/11WC-14-2_.jpg.
40. DesLauriers, P. J., Rohlfing, D. C. & Hsieh, E. T. Quantifying short chain branching microstructures in ethylene 1-olefin copolymers using size exclusion chromatography and fourier transform infrared spectroscopy (SEC-FTIR). *Polymer (Guildf).* **43**, 159–170 (2001).

41. Yu, Y. A Short-Chain Branching Distribution Determination Technique for Polyethylene Using IR5-Detected GPC. *Macromol. Symp.* **390**, 1–10 (2020).
42. Ahmadi, M., Nekoomanesh, M. & Arabi, H. New approach in modeling of metallocenecatalyzed olefin polymerization using artificial neural networks. *Macromol. Theory Simulations* **18**, 195–200 (2009).
43. Charoenpanich, Thanutchoke; Anantawaraskul Siripon; Soares, J. B. P. Using Artificial Intelligence Techniques to Design Ethylene/1-Olefin Copolymers. *Macromol. Theory Simulations* **29**, 2000048 (2020).
44. Ishola, N. B. & McKenna, T. F. L. Influence of Process Parameters on the Gas Phase Polymerization of Ethylene: RSM or ANN Statistical Methods? *Macromol. Theory Simulations* **2100059**, 2100059 (2021).
45. scipy.optimize.minimize — SciPy v1.7.1 Manual. https://docs.scipy.org/doc/scipy/reference/generated/scipy.optimize.minimize.html.

Appendix A: Polymerization Synthesis Conditions of DoE runs, and validation runs

ID	Run #	E (mol/L)	R	T (°C)	PC2 (psig)	1-Hexene (g)
0	1	0.60	0.400	120	170	3.78
4	2	0.63	0.524	110	160	5.17
13	3	0.34	0.280	130	110	1.45
15	4	0.64	0.000	130	200	0
12	5	0.41	0.800	128	130	5.25
10	6	0.34	0.496	121	100	2.40
0	7	0.60	0.400	120	170	3.80
5	8	0.35	0.668	110	90	3.54
6	9	0.81	0.800	112	210	10.88
14	10	0.84	0.668	130	260	9.75
3	11	0.86	0.276	110	220	3.79
8	12	0.35	0.000	119	100	0
14	13	0.84	0.668	130	260	9.75
15	14	0.64	0.000	130	200	0
1	15	0.55	0.000	110	140	0
2	16	0.35	0.240	110	90	1.27
12	17	0.41	0.800	128	130	5.25
11	18	0.85	0.000	122	240	0
0	19	0.60	0.400	120	170	3.78
7	20	0.54	0.800	118	150	6.92
6	21	0.81	0.800	112	210	10.88
9	22	0.86	0.528	120	240	7.54

Appendix B: 2-site and 3-site Deconvolution Fits

Run	SSE 2-site	SSE 3-site	Parameters[A] 2-site	Parameters[B] 3-site
1	0.023476	0.054098	[0.55, 0.45, 12624, 6106]	[0.03, 0.48, 0.49, 161411210, 6492, 12782]
10	0.034569	0.013298	[0.33, 0.67, 4556, 10234]	[0.49, 0.06, 0.44, 6396, 2756, 11610]
11	0.06515	0.045494	[0.2, 0.8, 23040, 9236]	[0.01, 0.77, 0.22, 103731514, 9116, 20500]
12	0.06985	0.017786	[0.22, 0.78, 4070, 10768]	[0.22, 0.09, 0.69, 16256, 2868, 8490]
13	0.054089	0.029092	[0.67, 0.33, 10234, 4556]	[0.44, 0.06, 0.49, 11610, 2756, 6396]
14	0.033152	0.029897	[0.34, 0.66, 5352, 11522]	[0.59, 0.4, 0.02, 11904, 5964, 898]
15	0.074458	0.074458	[0.62, 0.38, 8590, 17276]	[0.25, 0.13, 0.62, 17276, 17276, 8588]
17	0.036561	0.022171	[0.4, 0.6, 4584, 9152]	[0.08, 0.74, 0.18, 2802, 6644, 12872]
18	0.045386	0.077622	[0.48, 0.52, 13758, 7468]	[0.43, 0.02, 0.55, 13868, 2214194558, 7772]
19	0.051613	0.08377	[0.45, 0.55, 6106, 12624]	[0.48, 0.49, 0.03, 6492, 12782, 989615880]
2	0.017088	0.028436	[0.46, 0.54, 6900, 13564]	[0.02, 0.51, 0.47, 66223444, 13582, 7086]
20	0.077233	0.078283	[0.44, 0.56, 5564, 11474]	[0.02, 0.46, 0.52, 110696922, 5802, 11518]
21	0.032295	0.011383	[0.24, 0.76, 4848, 11088]	[0.43, 0.53, 0.04, 13208, 7456, 2442]
22	0.062166	0.052981	[0.27, 0.73, 4986, 11058]	[0.59, 0.36, 0.05, 7622, 13728, 2638]
3	0.037378	0.014169	[0.24, 0.76, 3502, 8816]	[0.09, 0.14, 0.77, 16088, 2906, 7766]
4	0.048074	0.021509	[0.34, 0.66, 5352, 11522]	[0.59, 0.02, 0.4, 11904, 898, 5964]
5	0.063323	0.067074	[0.4, 0.6, 4584, 9152]	[0.18, 0.74, 0.08, 12870, 6644, 2802]
6	0.041457	0.027348	[0.29, 0.71, 4244, 9680]	[0.1, 0.6, 0.3, 3010, 7160, 12244]
7	0.029261	0.030219	[0.45, 0.55, 6106, 12624]	[0.5, 0.01, 0.49, 6492, 1110, 13040]
8	0.12544	0.121627	[0.29, 0.71, 4894, 10582]	[0.31, 0.01, 0.68, 5208, 1716, 10714]
9	0.036163	0.016317	[0.76, 0.24, 11088, 4848]	[0.04, 0.53, 0.43, 2442, 7456, 13208]
16	0.2049	0.1985	[0.746, 0.254, 11504, 4994]	[0.039, 0.534, 0.426, 2609, 12831, 7046]

[A]: [m_1, m_2, Mw_1, Mw_2]

[B]: [m_1, m_2, m_3, Mw_1, Mw_2, Mw_3]

Average SSE: 2-site= 5.74×10^{-2}

Average SSE: 3-site= 5.55×10^{-2}

Appendix C: Lack of Fit Tests

Slice#	log M	F*	F-crit	MSLF	MSPE	p-value
1	2.9000	1.48	7.56	5.61×10^{-4}	3.80×10^{-4}	0.33
2	2.9177	1.69	7.56	6.01×10^{-4}	3.56×10^{-4}	0.268
3	2.9354	1.95	7.56	6.48×10^{-4}	3.32×10^{-4}	0.21
4	2.953	2.29	7.56	7.01×10^{-4}	3.06×10^{-4}	0.157
5	2.9707	2.71	7.56	7.60×10^{-4}	2.80×10^{-4}	0.112
6	2.9884	3.21	7.56	8.25×10^{-4}	2.57×10^{-4}	0.079
7	3.0061	1.15	7.66	2.68×10^{-4}	2.33×10^{-4}	0.458
8	3.0237	1.29	7.66	2.71×10^{-4}	2.11×10^{-4}	0.398
9	3.0414	1.45	7.66	2.77×10^{-4}	1.91×10^{-4}	0.337
10	3.0591	1.65	7.66	2.85×10^{-4}	1.72×10^{-4}	0.277
11	3.0768	1.89	7.66	2.95×10^{-4}	1.56×10^{-4}	0.223
12	3.0944	2.23	7.66	3.08×10^{-4}	1.38×10^{-4}	0.166
13	3.1121	2.63	7.66	3.19×10^{-4}	1.21×10^{-4}	0.121
14	3.1298	3.11	7.66	3.31×10^{-4}	1.06×10^{-4}	0.086
15	3.1475	3.66	7.66	3.45×10^{-4}	9.41×10^{-5}	0.06
16	3.1652	2.87	7.72	2.47×10^{-4}	8.59×10^{-5}	0.102
17	3.1828	3.21	7.72	2.49×10^{-4}	7.75×10^{-5}	0.081
18	3.2005	3.64	7.72	2.52×10^{-4}	6.92×10^{-5}	0.062
19	3.2182	4.12	7.72	2.59×10^{-4}	6.29×10^{-5}	0.047
20	3.2359	4.57	7.72	2.68×10^{-4}	5.85×10^{-5}	0.037
21	3.2535	4.98	7.72	2.78×10^{-4}	5.58×10^{-5}	0.03
22	3.2712	5.4	7.72	2.89×10^{-4}	5.36×10^{-5}	0.025
23	3.2889	5.72	7.72	3.04×10^{-4}	5.31×10^{-5}	0.021
24	3.3066	5.97	7.72	3.24×10^{-4}	5.42×10^{-5}	0.019
25	3.3242	6.17	7.72	3.51×10^{-4}	5.68×10^{-5}	0.018
26	3.3419	6.51	7.72	3.87×10^{-4}	5.94×10^{-5}	0.015
27	3.3596	6.86	7.72	4.31×10^{-4}	6.28×10^{-5}	0.014
28	3.3773	7.33	7.72	4.89×10^{-4}	6.67×10^{-5}	0.011
29	3.3949	6.18	7.72	4.45×10^{-4}	7.21×10^{-5}	0.018
30	3.4126	4.37	7.79	3.47×10^{-4}	7.93×10^{-5}	0.041
31	3.4303	4.56	7.79	3.95×10^{-4}	8.66×10^{-5}	0.038
32	3.448	5.73	7.72	5.42×10^{-4}	9.46×10^{-5}	0.021
33	3.4657	5.48	7.72	5.64×10^{-4}	1.03×10^{-4}	0.024
34	3.4833	5.33	7.72	5.89×10^{-4}	1.11×10^{-4}	0.025
35	3.501	5.21	7.72	6.19×10^{-4}	1.19×10^{-4}	0.027
36	3.5187	5.15	7.72	6.57×10^{-4}	1.28×10^{-4}	0.028
37	3.5364	5.19	7.72	7.05×10^{-4}	1.36×10^{-4}	0.027
38	3.554	5.29	7.72	7.63×10^{-4}	1.44×10^{-4}	0.026
39	3.5717	7.38	7.66	1.13×10^{-3}	1.54×10^{-4}	0.011
40	3.5894	6.97	7.66	1.14×10^{-3}	1.64×10^{-4}	0.013
41	3.6071	6.35	7.66	1.12×10^{-3}	1.77×10^{-4}	0.016
42	3.6247	5.94	7.66	1.12×10^{-3}	1.88×10^{-4}	0.019
43	3.6424	2.72	7.79	5.42×10^{-4}	1.99×10^{-4}	0.115

44	3.6601	4.95	7.66	1.04×10^{-3}	2.10×10^{-4}	0.03
45	3.6778	4.86	7.66	1.08×10^{-3}	2.22×10^{-4}	0.031
46	3.6955	5.02	7.66	1.16×10^{-3}	2.31×10^{-4}	0.029
47	3.7131	5.48	7.66	1.30×10^{-3}	2.37×10^{-4}	0.023
48	3.7308	3.89	7.72	9.48×10^{-4}	2.44×10^{-4}	0.053
49	3.7485	3.65	7.72	9.17×10^{-4}	2.51×10^{-4}	0.061
50	3.7662	3.41	7.72	8.96×10^{-4}	2.63×10^{-4}	0.071
51	3.7838	3.82	7.72	1.03×10^{-3}	2.69×10^{-4}	0.056
52	3.8015	3.74	7.72	1.02×10^{-3}	2.72×10^{-4}	0.058
53	3.8192	4.91	7.66	1.35×10^{-3}	2.74×10^{-4}	0.031
54	3.8369	7.21	7.56	1.99×10^{-3}	2.76×10^{-4}	0.011
55	3.8545	5.37	7.56	1.54×10^{-3}	2.87×10^{-4}	0.024
56	3.8722	4.24	7.56	1.23×10^{-3}	2.89×10^{-4}	0.042
57	3.8899	3.69	7.56	1.07×10^{-3}	2.90×10^{-4}	0.058
58	3.9076	3.75	7.56	1.10×10^{-3}	2.93×10^{-4}	0.056
59	3.9253	4.39	7.56	1.31×10^{-3}	2.99×10^{-4}	0.039
60	3.9429	5.52	7.56	1.73×10^{-3}	3.13×10^{-4}	0.022
61	3.9606	7.45	7.56	2.35×10^{-3}	3.15×10^{-4}	0.01
62	3.9783	10.03	7.56	3.15×10^{-3}	3.14×10^{-4}	0.005
63	3.996	9.31	7.6	2.94×10^{-3}	3.15×10^{-4}	0.006
64	4.0136	11.13	7.6	3.60×10^{-3}	3.23×10^{-4}	0.004
65	4.0313	5.9	7.72	1.97×10^{-3}	3.34×10^{-4}	0.02
66	4.049	6.08	7.72	2.04×10^{-3}	3.36×10^{-4}	0.018
67	4.0667	6.29	7.72	2.10×10^{-3}	3.34×10^{-4}	0.017
68	4.0843	6.42	7.72	2.14×10^{-3}	3.34×10^{-4}	0.016
69	4.102	6.4	7.72	2.16×10^{-3}	3.38×10^{-4}	0.016
70	4.1197	6.48	7.72	2.17×10^{-3}	3.35×10^{-4}	0.016
71	4.1374	6.67	7.72	2.18×10^{-3}	3.27×10^{-4}	0.015
72	4.1551	4.73	7.79	1.50×10^{-3}	3.16×10^{-4}	0.034
73	4.1727	4.63	7.79	1.42×10^{-3}	3.07×10^{-4}	0.036
74	4.1904	4.53	7.79	1.35×10^{-3}	2.99×10^{-4}	0.038
75	4.2081	4.53	7.79	1.29×10^{-3}	2.85×10^{-4}	0.038
76	4.2258	4.61	7.79	1.24×10^{-3}	2.69×10^{-4}	0.037
77	4.2434	4.9	7.79	1.23×10^{-3}	2.50×10^{-4}	0.032
78	4.2611	5.13	7.79	1.19×10^{-3}	2.31×10^{-4}	0.028
79	4.2788	5.44	7.79	1.16×10^{-3}	2.13×10^{-4}	0.025
80	4.2965	5.25	7.79	1.02×10^{-3}	1.94×10^{-4}	0.027
81	4.3141	5.71	7.79	9.97×10^{-4}	1.75×10^{-4}	0.022
82	4.3318	6.25	7.79	9.82×10^{-4}	1.57×10^{-4}	0.018
83	4.3495	6.94	7.79	9.77×10^{-4}	1.41×10^{-4}	0.013
84	4.3672	3.79	7.87	4.63×10^{-4}	1.22×10^{-4}	0.058
85	4.3848	3.97	7.87	4.22×10^{-4}	1.06×10^{-4}	0.053
86	4.4025	4.3	7.87	4.00×10^{-4}	9.30×10^{-5}	0.044
87	4.4202	4.71	7.87	3.88×10^{-4}	8.23×10^{-5}	0.036
88	4.4379	5.45	7.87	3.84×10^{-4}	7.05×10^{-5}	0.025
89	4.4556	6.61	7.87	3.91×10^{-4}	5.91×10^{-5}	0.016

90	4.4732	7.93	7.87	4.03×10^{-4}	5.08×10^{-5}	0.01
91	4.4909	9.47	7.87	4.15×10^{-4}	4.38×10^{-5}	0.006
92	4.5086	10.75	7.87	4.25×10^{-4}	3.95×10^{-5}	0.004
93	4.5263	12.63	7.87	4.30×10^{-4}	3.40×10^{-5}	0.003
94	4.5439	14.71	7.87	4.30×10^{-4}	2.92×10^{-5}	0.002
95	4.5616	21.99	7.79	5.92×10^{-4}	2.69×10^{-5}	0.001
96	4.5793	23.11	7.72	5.76×10^{-4}	2.49×10^{-5}	<0.001
97	4.597	84.55	7.56	2.01×10^{-3}	2.38×10^{-5}	<0.001
98	4.6146	70.26	7.56	1.57×10^{-3}	2.23×10^{-5}	<0.001
99	4.6323	57.72	7.56	1.21×10^{-3}	2.09×10^{-5}	<0.001
100	4.6500	45.04	7.56	9.27×10^{-4}	2.06×10^{-5}	<0.001

The lack of fit is significant in the slices # 62-64 and 90-100

Appendix D: Regression and ANOVA Tables

SS: Sum of squares

MS: Mean square

df: degrees of freedom

Slice # 1 (log M= 2.9)

Regression Statistics	
R Square	0.928
Adjusted R Square	0.880
Standard Error	0.023
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.138	0.138	270.9	4.299E-13
Residual	21	0.011	0.001		
Total	22	0.148			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	5.431E-06	3.300E-07	1.646E+01	1.776E-13	4.745E-06	6.118E-06

Slice # 2 (log M= 2.9176)

Regression Statistics	
R Square	0.935
Adjusted R Square	0.888

Standard Error	0.023
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.161	0.161	303.3	1.491E-13
Residual	21	0.011	0.001		
Total	22	0.172			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	5.874E-06	3.373E-07	1.741E+01	5.859E-14	5.172E-06	6.575E-06

Slice # 3 (log M= 2.9353)

Regression Statistics	
R Square	0.941
Adjusted R Square	0.894
Standard Error	0.024
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.188	0.188	337.1	5.498E-14
Residual	21	0.012	0.001		
Total	22	0.200			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*

T^2	6.343E-06	3.455E-07	1.836E+01	2.062E-14	5.625E-06	7.062E-06

Slice # 4 (log M= 2.9530)

Regression Statistics	
R Square	0.947
Adjusted R Square	0.899
Standard Error	0.024
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.219	0.219	371.9	2.161E-14
Residual	21	0.012	0.001		
Total	22	0.231			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	6.840E-06	3.547E-07	1.929E+01	7.757E-15	6.103E-06	7.578E-06

Slice # 5 (log M= 2.9707)

Regression Statistics	
R Square	0.951
Adjusted R Square	0.903
Standard Error	0.025
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.254	0.254	406.9	9.168E-15

Residual	21	0.013	0.001
Total	22	0.267	

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	7.367E-06	3.652E-07	2.017E+01	3.159E-15	6.607E-06	8.126E-06

Slice # 6 (log M= 2.9884)

Regression Statistics	
R Square	0.955
Adjusted R Square	0.907
Standard Error	0.026
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.293	0.293	442.2	4.139E-15
Residual	21	0.014	0.001		
Total	22	0.307			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	7.922E-06	3.767E-07	2.103E+01	1.373E-15	7.139E-06	8.706E-06

Slice # 7 (log M= 3.0060)

Regression Statistics	
R Square	0.986
Adjusted R Square	0.932
Standard Error	0.016

Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.348	0.116	452.1	3.976E-17
Residual	19	0.005	0.000		
Total	22	0.353			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	1.003E-05	7.657E-07	1.311E+01	5.770E-11	8.432E-06	1.164E-05
TR	4.523E-04	9.602E-05	4.711E+00	1.523E-04	2.513E-04	6.533E-04
E	-7.661E-02	1.668E-02	-4.592E+00	1.991E-04	-1.115E-01	-4.169E-02

Slice # 8 (log M= 3.0237)

Regression Statistics	
R Square	0.988
Adjusted R Square	0.934
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.400	0.133	528.9	9.854E-18
Residual	19	0.005	2.523E-04		
Total	22	0.405			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*

T^2	1.069E-05	7.591E-07	1.409E+01	1.651E-11	9.105E-06	1.228E-05
TR	4.820E-04	9.520E-05	5.063E+00	6.902E-05	2.828E-04	6.813E-04
E	-8.017E-02	1.654E-02	-4.847E+00	1.120E-04	-1.148E-01	-4.555E-02

Slice # 9 (log M= 3.0414)

Regression Statistics	
R Square	0.990
Adjusted R Square	0.936
Standard Error	0.016
Observations	22

ANOVA

	df	***SS***	***MS***	***F***	***Significance F***
Regression	3	0.459	0.153	613.0	2.652E-18
Residual	19	0.005	2.498E-04		
Total	22	0.464			

	Coefficients	***Standard Error***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***
T^2	1.139E-05	7.552E-07	1.508E+01	5.023E-12	9.806E-06	1.297E-05
TR	5.121E-04	9.471E-05	5.407E+00	3.227E-05	3.139E-04	7.103E-04
E	-8.377E-02	1.646E-02	-5.091E+00	6.491E-05	-1.182E-01	-4.933E-02

Slice # 10 (log M= 3.0591)

Regression Statistics	
R Square	0.991
Adjusted R Square	0.938
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.526	0.175	703.2	7.795E-19
Residual	19	0.005	2.492E-04		
Total	22	0.531			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	1.212E-05	7.544E-07	1.606E+01	1.649E-12	1.054E-05	1.369E-05
TR	5.426E-04	9.461E-05	5.735E+00	1.584E-05	3.445E-04	7.406E-04
E	-8.737E-02	1.644E-02	-5.315E+00	3.956E-05	-1.218E-01	-5.296E-02

Slice # 11 (log M= 3.0768)

Regression Statistics	
R Square	0.992
Adjusted R Square	0.939
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.601	0.200	797.6	2.533E-19
Residual	19	0.005	2.511E-04		
Total	22	0.606			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	1.288E-05	7.573E-07	1.701E+01	5.906E-13	1.130E-05	1.447E-05

TR	5.754E-04	9.497E-05	6.059E+00	7.925E-06	3.767E-04	7.742E-04
E	-9.120E-02	1.650E-02	-5.526E+00	2.487E-05	-1.257E-01	-5.666E-02

Slice # 12 (log M= 3.0944)

Regression Statistics	
R Square	0.993
Adjusted R Square	0.940
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.686	0.229	900.1	8.598E-20
Residual	19	0.005	2.539E-04		
Total	22	0.690			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	1.369E-05	7.614E-07	1.797E+01	2.198E-13	1.209E-05	1.528E-05
TR	6.092E-04	9.549E-05	6.380E+00	4.048E-06	4.093E-04	8.090E-04
E	-9.501E-02	1.659E-02	-5.727E+00	1.612E-05	-1.297E-01	-6.029E-02

Slice # 13 (log M= 3.1121)

Regression Statistics	
R Square	0.994
Adjusted R Square	0.941
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.780	0.260	1015.6	2.923E-20
Residual	19	4.867E-03	2.561E-04		
Total	22	0.785			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	1.484E-05	8.076E-07	1.837E+01	1.484E-13	1.315E-05	1.653E-05
TR	6.284E-04	9.566E-05	6.569E+00	2.740E-06	4.282E-04	8.286E-04
ET	-8.689E-04	1.461E-04	-5.949E+00	1.001E-05	-1.175E-03	-5.632E-04

Slice # 14 (log M= 3.1297)

Regression Statistics	
R Square	0.994
Adjusted R Square	0.941
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.887	0.296	1136.4	1.069E-20
Residual	19	4.942E-03	2.601E-04		
Total	22	0.892			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	1.575E-05	8.138E-07	1.935E+01	5.816E-14	1.404E-05	1.745E-05
TR	6.630E-04	9.640E-05	6.877E+00	1.467E-06	4.612E-04	8.647E-04

ET	-9.062E-04	1.472E-04	-6.157E+00	6.448E-06	-1.214E-03	-5.982E-04

Slice # 15 (log M= 3.1474)

Regression Statistics	
R Square	0.995
Adjusted R Square	0.942
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	1.006	0.335	1262.7	4.163E-21
Residual	19	5.046E-03	2.655E-04		
Total	22	1.011			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	1.669E-05	8.223E-07	2.030E+01	2.430E-14	1.497E-05	1.841E-05
TR	6.988E-04	9.741E-05	7.174E+00	8.133E-07	4.949E-04	9.027E-04
ET	-9.432E-04	1.487E-04	-6.342E+00	4.380E-06	-1.255E-03	-6.319E-04

Slice # 16 (log M= 3.1651)

Regression Statistics	
R Square	0.997
Adjusted R Square	0.941
Standard Error	0.014
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	1.141	0.285	1476.9	2.332E-21
Residual	18	3.476E-03	1.931E-04		
Total	22	1.144			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	2.415E-05	2.269E-06	1.065E+01	3.372E-09	1.939E-05	2.892E-05
TR	6.871E-04	8.457E-05	8.125E+00	1.964E-07	5.095E-04	8.648E-04
ET	-3.790E-03	9.458E-04	-4.008E+00	8.256E-04	-5.777E-03	-1.803E-03
E^2	2.808E-01	9.370E-02	2.997E+00	7.740E-03	8.394E-02	4.777E-01

Slice # 17 (log M= 3.1828)

Regression Statistics	
R Square	0.997
Adjusted R Square	0.941
Standard Error	0.014
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	1.289	0.322	1682.3	7.738E-22
Residual	18	3.449E-03	1.916E-04		
Total	22	1.293			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	2.565E-05	2.260E-06	1.135E+01	1.230E-09	2.090E-05	3.040E-05
TR	7.215E-04	8.425E-05	8.564E+00	9.162E-08	5.445E-04	8.985E-04

ET	-4.029E-03	9.421E-04	-4.277E+00	4.537E-04	-6.009E-03	-2.050E-03
E^2	3.010E-01	9.334E-02	3.225E+00	4.699E-03	1.049E-01	4.971E-01

Slice # 18 (log M= 3.2005)

Regression Statistics	
R Square	0.998
Adjusted R Square	0.942
Standard Error	0.014
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	1.454	0.364	1900.9	2.746E-22
Residual	18	3.443E-03	1.913E-04		
Total	22	1.458			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	2.719E-05	2.258E-06	1.204E+01	4.755E-10	2.245E-05	3.194E-05
TR	7.559E-04	8.417E-05	8.980E+00	4.549E-08	5.791E-04	9.327E-04
ET	-4.272E-03	9.413E-04	-4.538E+00	2.546E-04	-6.249E-03	-2.294E-03
E^2	3.216E-01	9.326E-02	3.449E+00	2.865E-03	1.257E-01	5.175E-01

Slice # 19 (log M= 3.2181)

Regression Statistics	
R Square	0.998
Adjusted R Square	0.942
Standard Error	0.014
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	1.637	0.409	2114.2	1.114E-22
Residual	18	3.484E-03	1.935E-04		
Total	22	1.640			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	2.878E-05	2.271E-06	1.267E+01	2.090E-10	2.401E-05	3.355E-05
TR	7.896E-04	8.467E-05	9.325E+00	2.590E-08	6.117E-04	9.674E-04
ET	-4.513E-03	9.469E-04	-4.766E+00	1.544E-04	-6.502E-03	-2.524E-03
E^2	3.422E-01	9.382E-02	3.648E+00	1.841E-03	1.451E-01	5.393E-01

Slice # 20 (log M= 3.2359)

Regression Statistics	
R Square	0.998
Adjusted R Square	0.942
Standard Error	0.014
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	1.840	0.460	2324.9	4.978E-23
Residual	18	3.561E-03	1.978E-04		
Total	22	1.843			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*

T^2	3.042E-05	2.296E-06	1.325E+01	1.010E-10	2.560E-05	3.524E-05
TR	8.245E-04	8.560E-05	9.632E+00	1.585E-08	6.447E-04	1.004E-03
ET	-4.757E-03	9.573E-04	-4.969E+00	9.927E-05	-6.768E-03	-2.746E-03
E^2	3.630E-01	9.484E-02	3.828E+00	1.233E-03	1.638E-01	5.623E-01

Slice # 21 (log M= 3.2535)

Regression Statistics	
R Square	0.998
Adjusted R Square	0.942
Standard Error	0.014
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	2.063	0.516	2529.8	2.432E-23
Residual	18	3.670E-03	2.039E-04		
Total	22	2.067			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	3.213E-05	2.331E-06	1.378E+01	5.277E-11	2.723E-05	3.702E-05
TR	8.601E-04	8.691E-05	9.896E+00	1.048E-08	6.775E-04	1.043E-03
ET	-5.007E-03	9.719E-04	-5.152E+00	6.684E-05	-7.049E-03	-2.966E-03
E^2	3.843E-01	9.629E-02	3.991E+00	8.576E-04	1.820E-01	5.866E-01

Slice # 22 (log M= 3.2712)

Regression Statistics	
R Square	0.998
Adjusted R Square	0.943

Standard Error	0.015
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	2.310	0.577	2741.3	1.230E-23
Residual	18	3.791E-03	2.106E-04		
Total	22	2.313			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	3.387E-05	2.369E-06	1.429E+01	2.880E-11	2.889E-05	3.884E-05
TR	8.967E-04	8.833E-05	1.015E+01	7.082E-09	7.111E-04	1.082E-03
ET	-5.257E-03	9.878E-04	-5.322E+00	4.648E-05	-7.332E-03	-3.182E-03
E^2	4.056E-01	9.787E-02	4.145E+00	6.088E-04	2.000E-01	6.112E-01

Slice # 23 (log M= 3.2889)

Regression Statistics	
R Square	0.998
Adjusted R Square	0.943
Standard Error	0.015
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	2.579	0.645	2929.4	7.007E-24
Residual	18	3.962E-03	2.201E-04		

Total	22	2.583

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	3.566E-05	2.422E-06	1.472E+01	1.762E-11	3.057E-05	4.075E-05
TR	9.323E-04	9.030E-05	1.033E+01	5.446E-09	7.426E-04	1.122E-03
ET	-5.511E-03	1.010E-03	-5.458E+00	3.485E-05	-7.633E-03	-3.390E-03
E^2	4.277E-01	1.000E-01	4.275E+00	4.558E-04	2.175E-01	6.379E-01

Slice # 24 (log M= 3.3066)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.015
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	2.874	0.719	3073.6	4.659E-24
Residual	18	4.208E-03	2.338E-04		
Total	22	2.878			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	3.751E-05	2.496E-06	1.503E+01	1.251E-11	3.226E-05	4.275E-05
TR	9.664E-04	9.305E-05	1.038E+01	4.978E-09	7.709E-04	1.162E-03
ET	-5.768E-03	1.041E-03	-5.543E+00	2.910E-05	-7.955E-03	-3.582E-03
E^2	4.500E-01	1.031E-01	4.365E+00	3.732E-04	2.334E-01	6.667E-01

Slice # 25 (log M= 3.3242)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	3.194	0.799	3161.2	3.671E-24
Residual	18	4.547E-03	2.526E-04		
Total	22	3.199			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	3.939E-05	2.595E-06	1.518E+01	1.056E-11	3.394E-05	4.484E-05
TR	1.000E-03	9.674E-05	1.034E+01	5.338E-09	7.969E-04	1.203E-03
ET	-6.023E-03	1.082E-03	-5.568E+00	2.763E-05	-8.296E-03	-3.751E-03
E^2	4.724E-01	1.072E-01	4.407E+00	3.398E-04	2.472E-01	6.976E-01

Slice # 26 (log M= 3.3419)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.017
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	3.542	0.885	3186.1	3.435E-24
Residual	18	5.002E-03	2.779E-04		
Total	22	3.547			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	4.133E-05	2.722E-06	1.519E+01	1.048E-11	3.561E-05	4.705E-05
TR	1.032E-03	1.015E-04	1.017E+01	6.838E-09	8.192E-04	1.245E-03
ET	-6.287E-03	1.135E-03	-5.541E+00	2.924E-05	-8.671E-03	-3.903E-03
E^2	4.957E-01	1.124E-01	4.409E+00	3.385E-04	2.595E-01	7.319E-01

Slice # 27 (log M= 3.3596)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.018
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	3.918	0.979	3178.9	3.501E-24
Residual	18	5.546E-03	3.081E-04		
Total	22	3.923			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	4.331E-05	2.866E-06	1.511E+01	1.135E-11	3.729E-05	4.933E-05
TR	1.064E-03	1.068E-04	9.962E+00	9.473E-09	8.398E-04	1.289E-03

ET	-6.554E-03	1.195E-03	-5.486E+00	3.283E-05	-9.064E-03	-4.044E-03
E^2	5.197E-01	1.184E-01	4.391E+00	3.526E-04	2.710E-01	7.684E-01

Slice # 28 (log M= 3.3773)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.019
Observations	22

ANOVA

	df	***SS***	***MS***	***F***	***Significance F***
Regression	4	4.322	1.081	3106.3	4.259E-24
Residual	18	6.262E-03	3.479E-04		
Total	22	4.329			

	Coefficients	***Standard Error***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***
T^2	4.531E-05	3.045E-06	1.488E+01	1.474E-11	3.891E-05	5.171E-05
TR	1.095E-03	1.135E-04	9.649E+00	1.543E-08	8.568E-04	1.334E-03
ET	-6.818E-03	1.269E-03	-5.371E+00	4.192E-05	-9.485E-03	-4.151E-03
E^2	5.439E-01	1.258E-01	4.324E+00	4.086E-04	2.796E-01	8.081E-01

Slice # 29 (log M= 3.3949)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.018
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	4.758	1.189	3706.8	9.504E-25
Residual	18	5.776E-03	3.209E-04		
Total	22	4.764			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	4.712E-05	2.925E-06	1.611E+01	3.884E-12	4.098E-05	5.327E-05
R	1.375E-01	1.306E-02	1.052E+01	4.048E-09	1.100E-01	1.649E-01
ET	-6.952E-03	1.221E-03	-5.695E+00	2.116E-05	-9.516E-03	-4.387E-03
E^2	5.507E-01	1.210E-01	4.550E+00	2.481E-04	2.964E-01	8.049E-01

Slice # 30 (log M= 3.4126)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.940
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	5.224	1.045	4139.9	2.675E-24
Residual	17	4.290E-03	2.524E-04		
Total	22	5.228			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	4.629E-05	2.758E-06	1.679E+01	5.132E-12	4.047E-05	5.211E-05
R	2.546E-01	3.979E-02	6.400E+00	6.592E-06	1.707E-01	3.386E-01
ET	-6.767E-03	1.091E-03	-6.201E+00	9.669E-06	-9.069E-03	-4.464E-03
E^2	6.024E-01	1.078E-01	5.586E+00	3.276E-05	3.749E-01	8.299E-01
ER	-1.905E-01	6.406E-02	-2.974E+00	8.509E-03	-3.257E-01	-5.538E-02

Slice # 31 (log M= 3.4303)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.940
Standard Error	0.017
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	5.718	1.144	3993.1	3.570E-24
Residual	17	4.869E-03	2.864E-04		
Total	22	5.723			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T^2	4.803E-05	2.938E-06	1.635E+01	7.834E-12	4.183E-05	5.423E-05
R	2.674E-01	4.238E-02	6.309E+00	7.848E-06	1.780E-01	3.568E-01
ET	-6.954E-03	1.162E-03	-5.982E+00	1.485E-05	-9.406E-03	-4.501E-03
E^2	6.256E-01	1.149E-01	5.446E+00	4.359E-05	3.832E-01	8.679E-01
ER	-2.058E-01	6.825E-02	-3.015E+00	7.797E-03	-3.498E-01	-6.179E-02

Slice # 32 (log M= 3.4480)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.020
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	6.242	1.561	3970.6	5.301E-25
Residual	18	7.075E-03	3.930E-04		
Total	22	6.249			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.305E-03	3.467E-04	1.819E+01	4.931E-13	5.577E-03	7.034E-03
TR	1.197E-03	1.199E-04	9.988E+00	9.094E-09	9.455E-04	1.449E-03
E	-8.538E-01	1.478E-01	-5.777E+00	1.787E-05	-1.164E+00	-5.433E-01
E^2	5.567E-01	1.240E-01	4.489E+00	2.839E-04	2.961E-01	8.172E-01

Slice # 33 (log M= 3.4657)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.020
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	6.802	1.700	4146.7	3.668E-25
Residual	18	7.382E-03	4.101E-04		
Total	22	6.809			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.476E-03	3.541E-04	1.829E+01	4.486E-13	5.732E-03	7.220E-03
TR	1.216E-03	1.224E-04	9.935E+00	9.876E-09	9.592E-04	1.474E-03
E	-8.448E-01	1.510E-01	-5.596E+00	2.606E-05	-1.162E+00	-5.276E-01
E^2	5.479E-01	1.267E-01	4.325E+00	4.078E-04	2.817E-01	8.140E-01

Slice # 34 (log M= 3.4833)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.021
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	7.395	1.849	4303.5	2.676E-25
Residual	18	7.733E-03	4.296E-04		
Total	22	7.403			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.642E-03	3.624E-04	1.833E+01	4.330E-13	5.881E-03	7.404E-03

TR	1.233E-03	1.253E-04	9.836E+00	1.152E-08	9.694E-04	1.496E-03
E	-8.322E-01	1.545E-01	-5.386E+00	4.061E-05	-1.157E+00	-5.076E-01
E^2	5.365E-01	1.297E-01	4.138E+00	6.182E-04	2.641E-01	8.089E-01

Slice # 35 (log M= 3.5010)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.021
Observations	22

ANOVA

	df	***SS***	***MS***	***F***	***Significance F***
Regression	4	8.024	2.006	4439.1	2.057E-25
Residual	18	8.135E-03	4.519E-04		
Total	22	8.033			

	Coefficients	***Standard Error***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***
T	6.801E-03	3.717E-04	1.830E+01	4.454E-13	6.020E-03	7.582E-03
TR	1.247E-03	1.285E-04	9.697E+00	1.430E-08	9.764E-04	1.517E-03
E	-8.152E-01	1.585E-01	-5.144E+00	6.810E-05	-1.148E+00	-4.822E-01
E^2	5.219E-01	1.330E-01	3.925E+00	9.933E-04	2.425E-01	8.013E-01

Slice # 36 (log M= 3.5187)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943

Standard Error	0.022
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	8.693	2.173	4520.5	1.762E-25
Residual	18	8.653E-03	4.807E-04		
Total	22	8.701			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.956E-03	3.834E-04	1.814E+01	5.144E-13	6.151E-03	7.762E-03
TR	1.258E-03	1.326E-04	9.489E+00	1.990E-08	9.795E-04	1.537E-03
E	-7.948E-01	1.635E-01	-4.863E+00	1.251E-04	-1.138E+00	-4.514E-01
E^2	5.052E-01	1.372E-01	3.683E+00	1.701E-03	2.170E-01	7.933E-01

Slice # 37 (log M= 3.5364)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.023
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	9.401	2.350	4563.2767	1.627E-25
Residual	18	9.271E-03	5.151E-04		

Total	22	9.411

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	7.102E-03	3.969E-04	1.790E+01	6.508E-13	6.268E-03	7.936E-03
TR	1.267E-03	1.372E-04	9.233E+00	3.004E-08	9.788E-04	1.555E-03
E	-7.692E-01	1.692E-01	-4.546E+00	2.503E-04	-1.125E+00	-4.137E-01
E^2	4.846E-01	1.420E-01	3.414E+00	3.096E-03	1.864E-01	7.829E-01

Slice # 38 (log M= 3.5540)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.943
Standard Error	0.024
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	10.153	2.538	4558.507937	1.641E-25
Residual	18	1.002E-02	5.568E-04		
Total	22	10.163			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	7.238E-03	4.126E-04	1.754E+01	9.155E-13	6.371E-03	8.105E-03
TR	1.274E-03	1.427E-04	8.927E+00	4.971E-08	9.739E-04	1.573E-03
E	-7.377E-01	1.759E-01	-4.193E+00	5.461E-04	-1.107E+00	-3.681E-01
E^2	4.600E-01	1.476E-01	3.116E+00	5.966E-03	1.498E-01	7.701E-01

Slice # 39 (log M= 3.5717)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.946
Standard Error	0.029
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	10.944	3.648	4425.5	5.385E-26
Residual	19	1.566E-02	8.244E-04		
Total	22	10.960			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.236E-03	1.761E-04	3.540E+01	8.198E-19	5.867E-03	6.605E-03
TR	1.316E-03	1.729E-04	7.611E+00	3.489E-07	9.538E-04	1.677E-03
E	-1.922E-01	3.142E-02	-6.119E+00	6.977E-06	-2.580E-01	-1.265E-01

Slice # 40 (log M= 3.5894)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.946
Standard Error	0.029
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	11.790	3.930	4716.3	3.039E-26
Residual	19	1.583E-02	8.333E-04		
Total	22	11.806			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.470E-03	1.811E-04	3.573E+01	6.911E-19	6.091E-03	6.849E-03
TR	1.299E-03	1.736E-04	7.480E+00	4.483E-07	9.353E-04	1.662E-03
ET	-1.601E-03	2.681E-04	-5.972E+00	9.529E-06	-2.162E-03	-1.040E-03

Slice # 41 (log M= 3.6071)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.946
Standard Error	0.029
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	12.683	4.228	5133.344677	1.419E-26
Residual	19	0.016	8.236E-04		
Total	22	12.699			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.685E-03	1.800E-04	3.714E+01	3.351E-19	6.309E-03	7.062E-03
TR	1.293E-03	1.726E-04	7.488E+00	4.415E-07	9.312E-04	1.654E-03

ET	-1.577E-03	2.665E-04	-5.916E+00	1.073E-05	-2.135E-03	-1.019E-03

Slice # 42 (log M= 3.6247)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.946
Standard Error	0.029
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	13.623	4.541	5513.3	7.469E-27
Residual	19	1.565E-02	8.237E-04		
Total	22	13.639			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.901E-03	1.800E-04	3.833E+01	1.847E-19	6.525E-03	7.278E-03
TR	1.282E-03	1.726E-04	7.426E+00	4.977E-07	9.205E-04	1.643E-03
ET	-1.544E-03	2.665E-04	-5.794E+00	1.394E-05	-2.102E-03	-9.865E-04

Slice # 43 (log M= 3.6424)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.941
Standard Error	0.021
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	14.616	2.923	6943.4	4.285E-26
Residual	17	7.157E-03	4.210E-04		
Total	22	14.623			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	7.938E-03	3.345E-04	2.373E+01	1.795E-14	7.232E-03	8.644E-03
TR	2.327E-03	4.062E-04	5.729E+00	2.460E-05	1.470E-03	3.184E-03
ET	-5.484E-03	1.096E-03	-5.003E+00	1.090E-04	-7.797E-03	-3.171E-03
E^2	4.900E-01	1.147E-01	4.273E+00	5.136E-04	2.481E-01	7.320E-01
ER	-2.306E-01	7.878E-02	-2.928E+00	9.392E-03	-3.969E-01	-6.444E-02

Slice # 44 (log M= 3.6601)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.946
Standard Error	0.028
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	15.632	5.211	6694.960609	1.303E-27
Residual	19	1.479E-02	7.783E-04		
Total	22	15.647			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.456E-03	8.780E-05	7.353E+01	8.485E-25	6.272E-03	6.640E-03
R	3.530E-01	4.154E-02	8.497E+00	6.767E-08	2.660E-01	4.399E-01
ER	-3.329E-01	5.789E-02	-5.751E+00	1.530E-05	-4.541E-01	-2.118E-01

Slice # 45 (log M= 3.6778)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.946
Standard Error	0.028
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	16.687	5.562	6896.6	9.980E-28
Residual	19	1.532E-02	8.066E-04		
Total	22	16.703			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.698E-03	8.938E-05	7.494E+01	5.925E-25	6.511E-03	6.885E-03
R	3.433E-01	4.229E-02	8.117E+00	1.349E-07	2.548E-01	4.318E-01
ER	-3.207E-01	5.894E-02	-5.441E+00	2.995E-05	-4.440E-01	-1.973E-01

Slice # 46 (log M= 3.6955)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.946

Standard Error	0.029
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	17.764	5.921	6836.6	1.080E-27
Residual	19	1.646E-02	8.661E-04		
Total	22	17.780			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	6.940E-03	9.263E-05	7.493E+01	5.935E-25	6.746E-03	7.134E-03
R	3.311E-01	4.382E-02	7.555E+00	3.882E-07	2.393E-01	4.228E-01
ER	-3.057E-01	6.107E-02	-5.006E+00	7.850E-05	-4.335E-01	-1.779E-01

Slice # 47 (log M= 3.7131)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.946
Standard Error	0.031
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	18.850	6.283	6530.5	1.630E-27
Residual	19	1.828E-02	9.621E-04		
Total	22	18.868			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	7.181E-03	9.763E-05	7.355E+01	8.427E-25	6.976E-03	7.385E-03
R	3.168E-01	4.619E-02	6.858E+00	1.525E-06	2.201E-01	4.134E-01
ER	-2.887E-01	6.437E-02	-4.485E+00	2.536E-04	-4.234E-01	-1.540E-01

Slice # 48 (log M= 3.7308)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.944
Standard Error	0.027
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	19.942	4.986	6990.8	4.346E-27
Residual	18	1.284E-02	7.132E-04		
Total	22	19.955			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	1.006E-02	7.825E-04	1.286E+01	1.646E-10	8.418E-03	1.171E-02
R	2.992E-01	3.977E-02	7.523E+00	5.811E-07	2.156E-01	3.827E-01
ER	-2.820E-01	5.553E-02	-5.078E+00	7.846E-05	-3.987E-01	-1.653E-01
T^2	-2.161E-05	6.356E-06	-3.399E+00	3.195E-03	-3.496E-05	-8.253E-06

Slice # 49 (log M= 3.7485)

Regression Statistics

R Square	0.999
Adjusted R Square	0.944
Standard Error	0.026
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	21.013	5.253	7561.4	2.232E-27
Residual	18	1.251E-02	6.947E-04		
Total	22	21.025			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	1.090E-02	7.723E-04	1.412E+01	3.535E-11	9.282E-03	1.253E-02
R	2.806E-01	3.925E-02	7.148E+00	1.172E-06	1.981E-01	3.630E-01
ER	-2.639E-01	5.481E-02	-4.815E+00	1.388E-04	-3.791E-01	-1.488E-01
T^2	-2.661E-05	6.273E-06	-4.241E+00	4.911E-04	-3.978E-05	-1.343E-05

Slice # 50 (log M= 3.7662)

Regression Statistics	
R Square	0.999
Adjusted R Square	0.944
Standard Error	0.026
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*

Regression	4	22.050	5.512	8052.5	1.308E-27
Residual	18	1.232E-02	6.846E-04		
Total	22	22.062			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
T	1.178E-02	7.667E-04	1.536E+01	8.661E-12	1.017E-02	1.339E-02
R	2.589E-01	3.896E-02	6.646E+00	3.087E-06	1.771E-01	3.408E-01
T^2	-3.191E-05	6.227E-06	-5.124E+00	7.106E-05	-4.499E-05	-1.882E-05
ER	-2.430E-01	5.441E-02	-4.467E+00	2.979E-04	-3.573E-01	-1.287E-01

Slice # 51 (log M= 3.7838)

Regression Statistics	
R Square	0.766
Adjusted R Square	0.727
Standard Error	0.028
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	4.557E-02	1.519E-02	19.63127963	6.608E-06
Residual	18	1.393E-02	7.738E-04		
Total	21	5.950E-02			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	6.315E-01	9.652E-02	6.543E+00	3.781E-06	4.287E-01	8.343E-01
TR	1.846E-03	3.346E-04	5.518E+00	3.071E-05	1.143E-03	2.549E-03
T	2.907E-03	8.032E-04	3.620E+00	1.959E-03	1.220E-03	4.595E-03
ER	-2.044E-01	5.667E-02	-3.607E+00	2.014E-03	-3.235E-01	-8.536E-02

Slice # 52 (log M= 3.8015)

Regression Statistics	
R Square	0.718
Adjusted R Square	0.671
Standard Error	0.028
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	3.525E-02	1.175E-02	15.3	3.442E-05
Residual	18	1.385E-02	7.694E-04		
Total	21	4.910E-02			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	7.050E-01	9.624E-02	7.326E+00	8.391E-07	5.028E-01	9.072E-01
TR	1.637E-03	3.337E-04	4.906E+00	1.139E-04	9.359E-04	2.338E-03
ER	-1.808E-01	5.651E-02	-3.200E+00	4.966E-03	-2.995E-01	-6.209E-02
T	2.503E-03	8.009E-04	3.126E+00	5.841E-03	8.208E-04	4.186E-03

Slice # 53 (log M= 3.8192)

Regression Statistics	
R Square	0.518
Adjusted R Square	0.467
Standard Error	0.032
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	2	2.055E-02	1.027E-02	10.2	9.774E-04
Residual	19	1.913E-02	1.007E-03		
Total	21	3.968E-02			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.028E+00	1.199E-02	8.569E+01	4.672E-26	1.002E+00	1.053E+00
TR	1.602E-03	3.725E-04	4.301E+00	3.855E-04	8.224E-04	2.382E-03
ER	-1.883E-01	6.300E-02	-2.990E+00	7.533E-03	-3.202E-01	-5.648E-02

Slice # 54 (log M= 3.8638)

Regression Statistics	
R Square	0
Adjusted R Square	0
Standard Error	0.038
Observations	22

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.076E+00	8E-03	130.4	4.924E-32	1.060E+00	1.094E+00

Slice # 55 (log M= 3.8545)

Regression Statistics	
R Square	0
Adjusted R Square	0
Standard Error	0.034
Observations	22

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.089E+00	7E-03	148.6	3.200E-33	1.075E+00	1.105E+00

Slice # 56 (log M= 3.8722)

Regression Statistics	
R Square	0
Adjusted R Square	0
Standard Error	0.030
Observations	22

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.099E+00	7E-03	166.7	2.842E-34	1.086E+00	1.114E+00

Slice # 57 (log M= 3.8899)

Regression Statistics	
R Square	0
Adjusted R Square	0
Standard Error	0.028
Observations	22

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.107E+00	6E-03	178.3	6.972E-35	1.094E+00	1.120E+00

Slice # 58 (log M= 3.9076)

Regression Statistics	
R Square	0

Adjusted R Square	0
Standard Error	0.029
Observations	22

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.111E+00	6E-03	176.9	8.221E-35	1.098E+00	1.124E+00

Slice # 59 (log M= 3.9253)

Regression Statistics	
R Square	0
Adjusted R Square	0
Standard Error	0.031
Observations	22

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.112E+00	7E-03	163.0	4.584E-35	1.097E+00	1.126E+00

Slice # 60 (log M= 3.9429)

Regression Statistics	
R Square	0
Adjusted R Square	0
Standard Error	0.036
Observations	22

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.109E+00	8E-03	143.0	7.114E-33	1.093E+00	1.125E+00

Slice # 61 (log M= 3.9606)

Regression Statistics	
R Square	0

Adjusted R Square	0
Standard Error	0.041
Observations	22

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.103E+00	9E-03	123.1	1.642E-31	1.084E+00	1.122E+00

Slice # 62 (log M= 3.9782)

Regression Statistics	
R Square	0
Adjusted R Square	0
Standard Error	0.047
Observations	22

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.093E+00	10E-03	106.1	3.729E-30	1.072E+00	1.115E+00

Slice # 63 (log M= 3.9960)

Regression Statistics	
R Square	0.324
Adjusted R Square	0.290
Standard Error	0.046
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	2.058E-02	2.058E-02	9.6	5.712E-03
Residual	20	4.298E-02	2.149E-03		
Total	21	6.356E-02			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Constant	1.325E+00	7.908E-02	1.675E+01	3.092E-13	1.160E+00	1.490E+00	1.160E+00	1.490E+00
T^2	-1.679E-05	5.427E-06	-3.095E+00	5.712E-03	-2.811E-05	-5.475E-06	-2.811E-05	-5.475E-06

Slice # 64 (log M= 4.0136)

Regression Statistics	
R Square	0.350
Adjusted R Square	0.317
Standard Error	0.051
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	2.814E-02	2.814E-02	10.8	3.744E-03
Residual	20	5.231E-02	2.615E-03		
Total	21	8.045E-02			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Constant	1.351E+00	8.724E-02	1.548E+01	1.345E-12	1.169E+00	1.532E+00	1.169E+00	1.532E+00
T^2	-1.964E-05	5.987E-06	-3.280E+00	3.744E-03	-3.213E-05	-7.149E-06	-3.213E-05	-7.149E-06

Slice # 65 (log M= 4.0313)

Regression Statistics	
R Square	0.742

Adjusted R Square	0.699
Standard Error	0.038
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.074	0.025	17.2	1.573E-05
Residual	18	0.026	1.425E-03		
Total	21	0.099			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.361E+00	6.613E-02	2.058E+01	5.896E-14	1.222E+00	1.500E+00
T^2	-2.454E-05	4.506E-06	-5.447E+00	3.563E-05	-3.401E-05	-1.508E-05
TR	-8.881E-04	2.273E-04	-3.907E+00	1.032E-03	-1.366E-03	-4.106E-04
ET	1.231E-03	3.507E-04	3.511E+00	2.497E-03	4.944E-04	1.968E-03

Slice # 66 (log M= 4.0490)

Regression Statistics	
R Square	0.779
Adjusted R Square	0.742
Standard Error	0.038
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.093	0.031	21.1	4.018E-06

Residual	18	2.651E-02	1.473E-03		
Total	21	0.120			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.378E+00	6.723E-02	2.049E+01	6.317E-14	1.237E+00	1.519E+00
T^2	-2.745E-05	4.580E-06	-5.993E+00	1.143E-05	-3.707E-05	-1.783E-05
TR	-1.012E-03	2.310E-04	-4.378E+00	3.625E-04	-1.497E-03	-5.261E-04
ET	1.379E-03	3.565E-04	3.868E+00	1.127E-03	6.300E-04	2.128E-03

Slice # 67 (log M= 4.0667)

Regression Statistics	
R Square	0.807
Adjusted R Square	0.775
Standard Error	0.039
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.114	0.038	25.1	1.200E-06
Residual	18	0.027	0.002		
Total	21	0.141			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.390E+00	6.813E-02	2.040E+01	6.816E-14	1.247E+00	1.533E+00
T^2	-3.017E-05	4.642E-06	-6.500E+00	4.115E-06	-3.992E-05	-2.042E-05
TR	-1.128E-03	2.341E-04	-4.820E+00	1.374E-04	-1.620E-03	-6.366E-04
ET	1.515E-03	3.613E-04	4.195E+00	5.445E-04	7.565E-04	2.275E-03

Slice # 68 (log M= 4.0843)

Regression Statistics	
R Square	0.829
Adjusted R Square	0.801
Standard Error	0.039
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.135	0.045	29.2	3.955E-07
Residual	18	0.028	0.002		
Total	21	0.163			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.398E+00	6.874E-02	2.034E+01	7.192E-14	1.254E+00	1.543E+00
T^2	-3.275E-05	4.683E-06	-6.993E+00	1.576E-06	-4.259E-05	-2.291E-05
TR	-1.236E-03	2.362E-04	-5.234E+00	5.607E-05	-1.733E-03	-7.402E-04
ET	1.646E-03	3.645E-04	4.516E+00	2.674E-04	8.803E-04	2.412E-03

Slice # 69 (log M= 4.1020)

Regression Statistics	
R Square	0.848
Adjusted R Square	0.823
Standard Error	0.039
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.156	0.052	33.5	1.405E-07
Residual	18	0.028	0.002		
Total	21	0.184			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.402E+00	6.905E-02	2.030E+01	7.445E-14	1.257E+00	1.547E+00
T^2	-3.514E-05	4.704E-06	-7.469E+00	6.431E-07	-4.502E-05	-2.525E-05
TR	-1.339E-03	2.373E-04	-5.644E+00	2.354E-05	-1.838E-03	-8.408E-04
ET	1.769E-03	3.661E-04	4.832E+00	1.336E-04	1.000E-03	2.539E-03

Slice # 70 (log M= 4.1197)

Regression Statistics	
R Square	0.863
Adjusted R Square	0.840
Standard Error	0.040
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.177	0.059	37.9	5.517E-08
Residual	18	0.028	0.002		
Total	21	0.205			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.401E+00	6.921E-02	2.025E+01	7.793E-14	1.256E+00	1.547E+00
T^2	-3.734E-05	4.715E-06	-7.919E+00	2.830E-07	-4.725E-05	-2.744E-05

TR	-1.435E-03	2.378E-04	-6.031E+00	1.057E-05	-1.934E-03	-9.348E-04
ET	1.881E-03	3.670E-04	5.127E+00	7.065E-05	1.110E-03	2.652E-03

Slice # 71 (log M= 4.1374)

Regression Statistics	
R Square	0.875
Adjusted R Square	0.855
Standard Error	0.040
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	0.198	0.066	42.1	2.422E-08
Residual	18	0.028	0.002		
Total	21	0.226			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.397E+00	6.930E-02	2.016E+01	8.383E-14	1.252E+00	1.543E+00
T^2	-3.937E-05	4.721E-06	-8.339E+00	1.351E-07	-4.929E-05	-2.945E-05
TR	-1.521E-03	2.381E-04	-6.385E+00	5.174E-06	-2.021E-03	-1.020E-03
ET	1.979E-03	3.675E-04	5.386E+00	4.055E-05	1.207E-03	2.751E-03

Slice # 72 (log M= 4.1551)

Regression Statistics	
R Square	0.925
Adjusted R Square	0.907
Standard Error	0.033
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.226	0.057	52.4	2.433E-09
Residual	17	0.018	0.001		
Total	21	0.245			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.417E+00	5.831E-02	2.429E+01	1.221E-14	1.294E+00	1.540E+00
T^2	-5.845E-05	6.956E-06	-8.402E+00	1.860E-07	-7.312E-05	-4.377E-05
TR	-1.494E-03	2.008E-04	-7.444E+00	9.598E-07	-1.918E-03	-1.071E-03
ET	8.800E-03	2.257E-03	3.900E+00	1.153E-03	4.039E-03	1.356E-02
E^2	-6.764E-01	2.245E-01	-3.013E+00	7.832E-03	-1.150E+00	-2.028E-01

Slice # 73 (log M= 4.1721)

Regression Statistics	
R Square	0.933
Adjusted R Square	0.917
Standard Error	0.032
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.244	0.061	59.3	9.251E-10
Residual	17	0.017	0.001		
Total	21	0.261			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.404E+00	5.690E-02	2.467E+01	9.447E-15	1.284E+00	1.524E+00
T^2	-6.051E-05	6.788E-06	-8.915E+00	8.109E-08	-7.484E-05	-4.619E-05
TR	-1.558E-03	1.959E-04	-7.952E+00	3.963E-07	-1.971E-03	-1.145E-03
ET	9.090E-03	2.202E-03	4.128E+00	7.028E-04	4.444E-03	1.374E-02
E^2	-6.981E-01	2.190E-01	-3.187E+00	5.394E-03	-1.160E+00	-2.360E-01

Slice # 74 (log M= 4.1904)

Regression Statistics	
R Square	0.940
Adjusted R Square	0.925
Standard Error	0.031
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.259	0.065	66.1	3.915E-10
Residual	17	0.017	0.001		
Total	21	0.276			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.386E+00	5.554E-02	2.496E+01	7.776E-15	1.269E+00	1.504E+00
T^2	-6.221E-05	6.625E-06	-9.390E+00	3.864E-08	-7.619E-05	-4.823E-05
TR	-1.612E-03	1.912E-04	-8.432E+00	1.772E-07	-2.016E-03	-1.209E-03
ET	9.329E-03	2.149E-03	4.341E+00	4.444E-04	4.795E-03	1.386E-02
E^2	-7.159E-01	2.138E-01	-3.349E+00	3.808E-03	-1.167E+00	-2.649E-01

Slice # 75 (log M= 4.2081)

Regression Statistics	
R Square	0.945
Adjusted R Square	0.932
Standard Error	0.031
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.271	0.068	72.5	1.879E-10
Residual	17	0.016	0.001		
Total	21	0.287			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.365E+00	5.427E-02	2.515E+01	6.867E-15	1.250E+00	1.479E+00
T^2	-6.358E-05	6.474E-06	-9.821E+00	2.018E-08	-7.723E-05	-4.992E-05
TR	-1.655E-03	1.868E-04	-8.858E+00	8.875E-08	-2.049E-03	-1.261E-03
ET	9.518E-03	2.100E-03	4.532E+00	2.948E-04	5.087E-03	1.395E-02
E^2	-7.305E-01	2.089E-01	-3.497E+00	2.763E-03	-1.171E+00	-2.897E-01

Slice # 76 (log M= 4.2258)

Regression Statistics	
R Square	0.948
Adjusted R Square	0.936
Standard Error	0.030
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.280	7.000E-02	77.9741939	1.049E-10
Residual	17	0.015	8.978E-04		
Total	21	0.295			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.339E+00	5.318E-02	2.518E+01	6.740E-15	1.227E+00	1.451E+00
T^2	-6.453E-05	6.343E-06	-1.017E+01	1.203E-08	-7.792E-05	-5.115E-05
TR	-1.687E-03	1.831E-04	-9.216E+00	5.056E-08	-2.073E-03	-1.301E-03
ET	9.643E-03	2.058E-03	4.686E+00	2.125E-04	5.301E-03	1.398E-02
E^2	-7.403E-01	2.047E-01	-3.616E+00	2.131E-03	-1.172E+00	-3.084E-01

Slice # 77 (log M= 4.2434)

Regression Statistics	
R Square	0.950
Adjusted R Square	0.938
Standard Error	0.030
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.285	0.071	80.9	7.811E-11
Residual	17	0.015	0.001		
Total	21	0.300			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*

Constant	2.242E+00	1.304E-01	1.720E+01	3.481E-12	1.967E+00	2.517E+00
T	-1.562E-02	1.511E-03	-1.034E+01	9.490E-09	-1.881E-02	-1.243E-02
TR	-1.706E-03	1.814E-04	-9.406E+00	3.768E-08	-2.089E-03	-1.323E-03
ET	9.716E-03	2.042E-03	4.759E+00	1.820E-04	5.408E-03	1.402E-02
E^2	-7.470E-01	2.031E-01	-3.678E+00	1.866E-03	-1.176E+00	-3.185E-01

Slice # 78 (log M= 4.2611)

Regression Statistics	
R Square	0.952
Adjusted R Square	0.941
Standard Error	0.029
Observations	22

ANOVA

	df	***SS***	***MS***	***F***	***Significance F***
Regression	4	0.287	0.072	84.5	5.505E-11
Residual	17	0.014	0.001		
Total	21	0.301			

	Coefficients	***Standard Error***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***
Constant	2.208E+00	1.279E-01	1.726E+01	3.285E-12	1.938E+00	2.478E+00
T	-1.565E-02	1.483E-03	-1.055E+01	6.997E-09	-1.878E-02	-1.252E-02
TR	-1.717E-03	1.780E-04	-9.644E+00	2.626E-08	-2.092E-03	-1.341E-03
ET	9.717E-03	2.004E-03	4.849E+00	1.503E-04	5.489E-03	1.394E-02
E^2	-7.473E-01	1.993E-01	-3.749E+00	1.599E-03	-1.168E+00	-3.267E-01

Slice # 79 (log M= 4.2788)

Regression Statistics

R Square	0.953
Adjusted R Square	0.942
Standard Error	0.029
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.285	7.119E-02	86.3	4.649E-11
Residual	17	0.014	8.250E-04		
Total	21	0.299			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	2.164E+00	1.262E-01	1.715E+01	3.629E-12	1.898E+00	2.430E+00
T	-1.557E-02	1.462E-03	-1.065E+01	6.112E-09	-1.866E-02	-1.249E-02
TR	-1.717E-03	1.756E-04	-9.778E+00	2.148E-08	-2.087E-03	-1.346E-03
ET	9.643E-03	1.976E-03	4.880E+00	1.410E-04	5.473E-03	1.381E-02
E^2	-7.417E-01	1.966E-01	-3.773E+00	1.518E-03	-1.156E+00	-3.269E-01

Slice # 80 (log M= 4.2965)

Regression Statistics	
R Square	0.958
Adjusted R Square	0.948
Standard Error	0.027
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.281	7.015E-02	96.5	1.885E-11
Residual	17	0.012	7.271E-04		
Total	21	0.293			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	2.203E+00	1.181E-01	1.865E+01	9.317E-13	1.954E+00	2.452E+00
T	-1.618E-02	1.362E-03	-1.188E+01	1.175E-09	-1.906E-02	-1.331E-02
R	-2.085E-01	1.998E-02	-1.044E+01	8.235E-09	-2.507E-01	-1.664E-01
ET	9.583E-03	1.853E-03	5.170E+00	7.682E-05	5.673E-03	1.349E-02
E^2	-7.369E-01	1.844E-01	-3.995E+00	9.363E-04	-1.126E+00	-3.478E-01

Slice # 81 (log M= 4.3141)

Regression Statistics	
R Square	0.958
Adjusted R Square	0.948
Standard Error	0.027
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.272	6.788E-02	96.0	1.956E-11
Residual	17	0.012	7.068E-04		
Total	21	0.284			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	2.138E+00	1.164E-01	1.836E+01	1.202E-12	1.892E+00	2.384E+00

T	-1.590E-02	1.343E-03	-1.184E+01	1.238E-09	-1.874E-02	-1.307E-02
R	-2.059E-01	1.970E-02	-1.045E+01	8.060E-09	-2.475E-01	-1.643E-01
ET	9.385E-03	1.827E-03	5.136E+00	8.256E-05	5.530E-03	1.324E-02
E^2	-7.220E-01	1.818E-01	-3.970E+00	9.885E-04	-1.106E+00	-3.383E-01

Slice # 82 (log M= 4.3318)

Regression Statistics	
R Square	0.957
Adjusted R Square	0.946
Standard Error	0.026
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.259	6.475E-02	93.8	2.374E-11
Residual	17	0.012	6.905E-04		
Total	21	0.271			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	2.063E+00	1.151E-01	1.792E+01	1.783E-12	1.820E+00	2.305E+00
T	-1.552E-02	1.328E-03	-1.169E+01	1.507E-09	-1.832E-02	-1.272E-02
R	-2.018E-01	1.947E-02	-1.036E+01	9.143E-09	-2.429E-01	-1.607E-01
ET	9.140E-03	1.806E-03	5.060E+00	9.670E-05	5.329E-03	1.295E-02
E^2	-7.034E-01	1.797E-01	-3.914E+00	1.118E-03	-1.083E+00	-3.242E-01

Slice # 83 (log M= 4.3495)

Regression Statistics	
R Square	0.955

Adjusted R Square	0.944
Standard Error	0.026
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.244	0.061	89.5	3.452E-11
Residual	17	0.012	0.001		
Total	21	0.256			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.979E+00	1.143E-01	1.731E+01	3.123E-12	1.738E+00	2.220E+00
T	-1.505E-02	1.319E-03	-1.141E+01	2.163E-09	-1.784E-02	-1.227E-02
R	-1.964E-01	1.934E-02	-1.015E+01	1.236E-08	-2.372E-01	-1.556E-01
ET	8.854E-03	1.795E-03	4.934E+00	1.259E-04	5.068E-03	1.264E-02
E^2	-6.819E-01	1.786E-01	-3.819E+00	1.374E-03	-1.059E+00	-3.051E-01

Slice # 84 (log M= 4.3672)

Regression Statistics	
R Square	0.977
Adjusted R Square	0.970
Standard Error	0.018
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*

Regression	5	0.233	0.047	138.8	1.364E-12
Residual	16	5.365E-03	3.353E-04		
Total	21	0.238			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.456E+00	1.126E-01	1.293E+01	6.919E-10	1.217E+00	1.695E+00
T	-1.161E-02	9.067E-04	-1.280E+01	8.022E-10	-1.353E-02	-9.684E-03
R	-8.245E-01	2.105E-01	-3.918E+00	1.227E-03	-1.271E+00	-3.784E-01
E	1.336E+00	1.710E-01	7.812E+00	7.545E-07	9.732E-01	1.698E+00
E^2	-9.085E-01	1.412E-01	-6.434E+00	8.257E-06	-1.208E+00	-6.092E-01
TR	5.222E-03	1.737E-03	3.006E+00	8.371E-03	1.539E-03	8.904E-03

Slice # 85 (log M= 4.3848)

Regression Statistics	
R Square	0.978
Adjusted R Square	0.971
Standard Error	0.017
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	0.214	0.043	140.9	1.212E-12
Residual	16	4.858E-03	3.036E-04		
Total	21	0.219			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.392E+00	1.072E-01	1.299E+01	6.436E-10	1.165E+00	1.620E+00
T	-1.128E-02	8.627E-04	-1.308E+01	5.851E-10	-1.311E-02	-9.455E-03

R	-8.388E-01	2.003E-01	-4.189E+00	6.949E-04	-1.263E+00	-4.143E-01
E	1.297E+00	1.627E-01	7.975E+00	5.779E-07	9.526E-01	1.642E+00
E^2	-8.857E-01	1.344E-01	-6.592E+00	6.192E-06	-1.171E+00	-6.009E-01
TR	5.405E-03	1.653E-03	3.271E+00	4.809E-03	1.902E-03	8.909E-03

Slice # 86 (log M= 4.4025)

Regression Statistics	
R Square	0.977
Adjusted R Square	0.970
Standard Error	0.017
Observations	22

ANOVA

	df	***SS***	***MS***	***F***	***Significance F***
Regression	5	0.194	0.03876428	136.0	1.597E-12
Residual	16	4.560E-03	2.850E-04		
Total	21	0.198			

	Coefficients	***Standard Error***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***
Constant	1.322E+00	1.038E-01	1.274E+01	8.653E-10	1.102E+00	1.542E+00
T	-1.088E-02	8.359E-04	-1.302E+01	6.245E-10	-1.266E-02	-9.112E-03
R	-8.457E-01	1.940E-01	-4.359E+00	4.873E-04	-1.257E+00	-4.344E-01
E	1.253E+00	1.576E-01	7.950E+00	6.012E-07	9.191E-01	1.587E+00
E^2	-8.586E-01	1.302E-01	-6.596E+00	6.151E-06	-1.135E+00	-5.827E-01
TR	5.536E-03	1.601E-03	3.457E+00	3.244E-03	2.142E-03	8.931E-03

Slice # 87 (log M= 4.4202)

Regression Statistics

R Square	0.975
Adjusted R Square	0.968
Standard Error	0.017
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	0.174	0.035	127.1	2.714E-12
Residual	16	4.371E-03	2.732E-04		
Total	21	0.178			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.249E+00	1.016E-01	1.229E+01	1.459E-09	1.034E+00	1.464E+00
T	-1.044E-02	8.184E-04	-1.276E+01	8.415E-10	-1.218E-02	-8.707E-03
R	-8.484E-01	1.900E-01	-4.466E+00	3.899E-04	-1.251E+00	-4.457E-01
E	1.205E+00	1.543E-01	7.810E+00	7.561E-07	8.782E-01	1.533E+00
E^2	-8.288E-01	1.274E-01	-6.503E+00	7.283E-06	-1.099E+00	-5.586E-01
TR	5.638E-03	1.568E-03	3.596E+00	2.419E-03	2.314E-03	8.961E-03

Slice # 88 (log M= 4.4379)

Regression Statistics	
R Square	0.973
Adjusted R Square	0.964
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	0.153	3.068E-02	115.0	5.867E-12
Residual	16	0.0042671	2.667E-04		
Total	21	0.158			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Constant	1.171E+00	1.004E-01	1.166E+01	3.125E-09	9.579E-01	1.384E+00
T	-9.938E-03	8.086E-04	-1.229E+01	1.454E-09	-1.165E-02	-8.224E-03
R	-8.418E-01	1.877E-01	-4.485E+00	3.752E-04	-1.240E+00	-4.439E-01
E	1.154E+00	1.525E-01	7.567E+00	1.133E-06	8.306E-01	1.477E+00
E^2	-7.963E-01	1.259E-01	-6.324E+00	1.012E-05	-1.063E+00	-5.294E-01
TR	5.666E-03	1.549E-03	3.657E+00	2.125E-03	2.382E-03	8.949E-03

Slice # 89 (log M= 4.4556)

Regression Statistics	
R Square	0.969
Adjusted R Square	0.959
Standard Error	0.016
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	0.134	2.673E-02	100.3	1.691E-11
Residual	16	4.263E-03	2.665E-04		
Total	21	0.138			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*

Constant	1.089E+00	1.004E-01	1.085E+01	8.731E-09	8.764E-01	1.302E+00
T	-9.385E-03	8.083E-04	-1.161E+01	3.311E-09	-1.110E-02	-7.671E-03
R	-8.254E-01	1.876E-01	-4.399E+00	4.480E-04	-1.223E+00	-4.276E-01
E	1.100E+00	1.524E-01	7.214E+00	2.064E-06	7.765E-01	1.423E+00
E^2	-7.620E-01	1.259E-01	-6.054E+00	1.674E-05	-1.029E+00	-4.952E-01
TR	5.618E-03	1.548E-03	3.629E+00	2.259E-03	2.336E-03	8.901E-03

Slice # 90 (log M=4.4732)

Regression Statistics	
R Square	0.964
Adjusted R Square	0.952
Standard Error	0.016
Observations	22

ANOVA

	df	***SS***	***MS***	***F***	***Significance F***
Regression	5	0.115	0.023	84.7	6.185E-11
Residual	16	4.333E-03	2.708E-04		
Total	21	0.119			

	Coefficients	***Standard Error***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***	***Lower 95.0%***	***Upper 95.0%***
Constant	1.007E+00	1.012E-01	9.954E+00	2.928E-08	7.929E-01	1.222E+00	7.929E-01	1.222E+00
T	-8.800E-03	8.148E-04	-1.080E+01	9.316E-09	-1.053E-02	-7.073E-03	-1.053E-02	-7.073E-03
R	-8.031E-01	1.891E-01	-4.246E+00	6.162E-04	-1.204E+00	-4.021E-01	-1.204E+00	-4.021E-01
E	1.040E+00	1.537E-01	6.765E+00	4.538E-06	7.138E-01	1.365E+00	7.138E-01	1.365E+00
E^2	-7.233E-01	1.269E-01	-5.700E+00	3.282E-05	-9.923E-01	-4.543E-01	-9.923E-01	-4.543E-01
TR	5.524E-03	1.561E-03	3.539E+00	2.728E-03	2.215E-03	8.834E-03	2.215E-03	8.834E-03

Slice # 91 (log M=4.4909)

Regression Statistics	
R Square	0.957
Adjusted R Square	0.943
Standard Error	0.017
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	9.700E-02	1.940E-02	70.4	2.554E-10
Residual	16	4.411E-03	2.757E-04		
Total	21	1.014E-01			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Constant	9.248E-01	1.021E-01	9.057E+00	1.070E-07	7.084E-01	1.141E+00	7.084E-01	1.141E+00
T	-8.188E-03	8.221E-04	-9.959E+00	2.906E-08	-9.931E-03	-6.445E-03	-9.931E-03	-6.445E-03
R	-7.758E-01	1.908E-01	-4.065E+00	8.999E-04	-1.180E+00	-3.712E-01	-1.180E+00	-3.712E-01
E	9.763E-01	1.550E-01	6.297E+00	1.063E-05	6.476E-01	1.305E+00	6.476E-01	1.305E+00
E^2	-6.817E-01	1.280E-01	-5.324E+00	6.844E-05	-9.531E-01	-4.103E-01	-9.531E-01	-4.103E-01
TR	5.392E-03	1.575E-03	3.423E+00	3.485E-03	2.053E-03	8.730E-03	2.053E-03	8.730E-03

Slice # 92 (log M=4.5086)

Regression Statistics	
R Square	0.948
Adjusted R Square	0.931
Standard Error	0.017
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	8.119E-02	1.624E-02	57.9	1.113E-09
Residual	16	4.486E-03	2.804E-04		
Total	21	8.567E-02			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Constant	8.461E-01	1.030E-01	8.216E+00	3.917E-07	6.278E-01	1.064E+00	6.278E-01	1.064E+00
T	-7.593E-03	8.291E-04	-9.158E+00	9.209E-08	-9.350E-03	-5.835E-03	-9.350E-03	-5.835E-03
R	-7.491E-01	1.925E-01	-3.892E+00	1.295E-03	-1.157E+00	-3.411E-01	-1.157E+00	-3.411E-01
E	9.132E-01	1.564E-01	5.841E+00	2.507E-05	5.818E-01	1.245E+00	5.818E-01	1.245E+00
E^2	-6.398E-01	1.291E-01	-4.955E+00	1.433E-04	-9.135E-01	-3.661E-01	-9.135E-01	-3.661E-01
TR	5.262E-03	1.588E-03	3.313E+00	4.400E-03	1.895E-03	8.629E-03	1.895E-03	8.629E-03

Slice # 93 (log M=4.5263)

Regression Statistics	
R Square	0.937
Adjusted R Square	0.917
Standard Error	0.017
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	6.702E-02	1.340E-02	47.7	4.766E-09
Residual	16	4.500E-03	2.813E-04		

Total	21	7.152E-02

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Constant	7.665E-01	1.031E-01	7.431E+00	1.424E-06	5.478E-01	9.851E-01	5.478E-01	9.851E-01
T	-6.975E-03	8.304E-04	-8.399E+00	2.931E-07	-8.735E-03	-5.215E-03	-8.735E-03	-5.215E-03
R	-7.149E-01	1.928E-01	-3.708E+00	1.908E-03	-1.123E+00	-3.062E-01	-1.123E+00	-3.062E-01
E	8.510E-01	1.566E-01	5.434E+00	5.513E-05	5.190E-01	1.183E+00	5.190E-01	1.183E+00
E^2	-5.983E-01	1.293E-01	-4.627E+00	2.799E-04	-8.725E-01	-3.242E-01	-8.725E-01	-3.242E-01
TR	5.067E-03	1.591E-03	3.185E+00	5.758E-03	1.694E-03	8.439E-03	1.694E-03	8.439E-03

Slice # 94 (log M=4.5439)

Regression Statistics	
R Square	0.924
Adjusted R Square	0.900
Standard Error	0.017
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	5.449E-02	1.090E-02	39.0	2.084E-08
Residual	16	4.472E-03	2.795E-04		
Total	21	5.896E-02			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Constant	6.877E-01	1.028E-01	6.689E+00	5.207E-06	4.697E-01	9.056E-01	4.697E-01	9.056E-01
T	-6.353E-03	8.278E-04	-7.675E+00	9.455E-07	-8.108E-03	-4.598E-03	-8.108E-03	-4.598E-03

R	-6.730E-01	1.921E-01	-3.503E+00	2.946E-03	-1.080E+00	-2.657E-01	-1.080E+00	-2.657E-01
E	7.911E-01	1.561E-01	5.068E+00	1.142E-04	4.601E-01	1.122E+00	4.601E-01	1.122E+00
E^2	-5.587E-01	1.289E-01	-4.334E+00	5.129E-04	-8.320E-01	-2.854E-01	-8.320E-01	-2.854E-01
TR	4.809E-03	1.586E-03	3.033E+00	7.918E-03	1.448E-03	8.171E-03	1.448E-03	8.171E-03

Slice # 95 (log M=4.5616)

Regression Statistics	
R Square	0.861
Adjusted R Square	0.828
Standard Error	0.020
Observations	22

ANOVA

	df	***SS***	***MS***	***F***	***Significance F***
Regression	4	4.139E-02	1.035E-02	26.4	4.280E-07
Residual	17	6.673E-03	3.925E-04		
Total	21	4.806E-02			

	Coefficients	***Standard Error***	***t Stat***	***P-value***	***Lower 95%***	***Upper 95%***	***Lower 95.0%***	***Upper 95.0%***
Constant	3.991E-01	8.406E-02	4.748E+00	1.863E-04	2.218E-01	5.765E-01	2.218E-01	5.765E-01
T	-3.790E-03	5.574E-04	-6.799E+00	3.098E-06	-4.966E-03	-2.614E-03	-4.966E-03	-2.614E-03
R	-8.151E-02	1.459E-02	-5.588E+00	3.264E-05	-1.123E-01	-5.074E-02	-1.123E-01	-5.074E-02
E	6.533E-01	1.822E-01	3.585E+00	2.283E-03	2.688E-01	1.038E+00	2.688E-01	1.038E+00
E^2	-4.597E-01	1.509E-01	-3.047E+00	7.278E-03	-7.780E-01	-1.415E-01	-7.780E-01	-1.415E-01

Slice # 96 (log M=4.5793)

Regression Statistics

R Square	0.974
Adjusted R Square	0.914
Standard Error	0.020
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	0.264	6.607E-02	168.3	1.972E-13
Residual	18	7.065E-03	3.925E-04		
Total	22	0.271			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
E	1.021E+00	1.129E-01	9.044E+00	4.095E-08	7.839E-01	1.258E+00	7.839E-01	1.258E+00
ET	-5.148E-03	8.775E-04	-5.867E+00	1.482E-05	-6.992E-03	-3.305E-03	-6.992E-03	-3.305E-03
E^2	-2.646E-01	4.350E-02	-6.083E+00	9.512E-06	-3.560E-01	-1.732E-01	-3.560E-01	-1.732E-01
R	-7.840E-02	1.426E-02	-5.497E+00	3.209E-05	-1.084E-01	-4.843E-02	-1.084E-01	-4.843E-02

Slice # 97 (log M=4.5970)

Regression Statistics	
R Square	0.852
Adjusted R Square	0.804
Standard Error	0.038
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*

Regression	1	0.174	0.174	120.4	6.485E-10
Residual	21	3.034E-02	1.445E-03		
Total	22	0.204			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
E	1.410E-01	1.285E-02	1.097E+01	3.716E-10	1.143E-01	1.677E-01	1.143E-01	1.677E-01

Slice # 98 (log M=4.6416)

Regression Statistics	
R Square	0.845
Adjusted R Square	0.798
Standard Error	0.034
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.129	0.129	114.8	9.794E-10
Residual	21	2.360E-02	1.124E-03		
Total	22	0.153			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
E	1.214E-01	1.133E-02	1.071E+01	5.710E-10	9.786E-02	1.450E-01	9.786E-02	1.450E-01

Slice # 99 (log M=4.6323)

Regression Statistics	
R Square	0.839
Adjusted R Square	0.791

Standard Error	0.029
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	9.511E-02	9.511E-02	109.4	1.479E-09
Residual	21	1.826E-02	8.694E-04		
Total	22	0.113			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
E	1.043E-01	9.968E-03	1.046E+01	8.775E-10	8.353E-02	1.250E-01	8.353E-02	1.250E-01

Slice # 100 (log M=4.6500)

Regression Statistics	
R Square	0.833
Adjusted R Square	0.785
Standard Error	0.026
Observations	22

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	6.984E-02	6.984E-02	104.5	2.182E-09
Residual	21	1.403E-02	6.683E-04		
Total	22	8.387E-02			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
E	8.934E-02	8.739E-03	1.022E+01	1.316E-09	7.116E-02	1.075E-01	7.116E-02	1.075E-01