

**NOVEL SOLVENT APPLICATION FOR THE FREE RADICAL SOLUTION
POLYMERIZATION OF STYRENE**

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CERTIFICATION

This is to certify that the Thesis:

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POLYMERIZATION OF STYRENE**

**Submitted to the
School of Postgraduate Studies
University of Lagos**

**For the award of the degree of
DOCTOR OF PHILOSOPHY (Ph.D.)
is a record of original research carried out**

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In the Department of Chemical and Petroleum Engineering

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DEDICATION

This thesis is dedicated to the memory of my late elder sister, Hajia Risikat Ayoka, whose role as regards my upbringing was sorely missed. May Allah in his infinite mercy forgive her all her sins, errors, mistakes, misdeeds and inadequacies while on earth. May He continue to overlook all her shortcomings, ease her affairs in the grave and finally grant her AL-JANNA FIRDOUS (paradise) as her everlasting dwelling place (ameen).

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ABSTRACT

Polystyrene (PS) is an aromatic thermoplastic polymer that has a wide range of industrial and household applications. It is a product of exothermic reaction and its synthesis is prone to reaction runaway phenomenon which is induced either by insufficient heat removal or sudden increase in the viscosity of the reaction mixture. Polymerization reactions in solvents media offer advantages for possible solutions, yet their efficiency and dynamics on the polymerization of styrene has not been fully explored. In this research, experimental study and the modelling of free radical solution homo-polymerization of styrene were conducted to explore the effects of different solvents on the conversion of the styrene monomer and the quality of the synthesized polystyrene (PS). Seven solvents with different polarity namely acetone, chloroform, benzene, toluene, ethyl acetate, dimethyl sulfoxide and acetonitrile were used in the study. Two initiators; benzoyl peroxide (BPO) and benzoyl peroxide blend with dicyclohexylphthalate (BPO Blend) were also selected after prior solubility and miscibility screening with the initiators and styrene monomer, respectively. The key parameters considered were the solvent type, volume ratio of monomer to solvents, reaction time and temperature. In consonance with the requirements of green and sustainable chemistry, biodiesel produced from waste cooking oil (WCO) and pawpaw seed oil (PSO) were investigated as possible bio-solvents. The individual and interactive effects of the three processing conditions (reaction temperature, reaction time and initiator concentration) on styrene monomer conversion were investigated through the Central Composite Design (CCD) model of the Response Surface Methodology (RSM) for the design of experiment, modeling and process optimization. The styrene monomer conversion was also observed to be solvent dependent. Reaction rate mechanisms to further understand the kinetics of the solvent effects (KSEs) especially on the reaction propagation step were also proposed. Correlation between the solvent parameters with conversion using the linear solvation energy relationship of Kamlet and Taft in an SPSS version 20.0 software environment indicates varying behaviour in the two initiators. For BPO, dipolarity / polarizability and Reichardt electrophilicity demonstrate the most positive effect on monomer conversion, while refractive index, dielectric constant and Lewis acid – base interactions between the solvent and initiator show negative effect. On the other hand, for the BPO blend, dipolarity/polarizability, electrophilicity, and Lewis acid – base interactions all show positive influence on conversion, while refractive index and dielectric constant have negative effect. Acetone was found to be the most suitable solvent in terms of styrene monomer conversion, ease of product separation and environmental consideration. Biodiesel was found to be a weak solvent for the styrene homo-polymerization compared to the hydrocarbon solvents. Kinetics analysis reveals a free radical mechanism as evidenced by the chemical reaction mode at low conversion and diffusion controlled phenomena at high conversion. RSM evaluation reveals that reaction temperature and initiator concentration were found to be linearly and interactively significant, while reaction temperature alone was found to be quadratically significant. The optimized conditions are reaction time of 30 minutes, reaction temperature of 120 °C, and initiator concentration of 0.1135 mol/L, with the corresponding monomer conversion of 76.82 % as compared to the observed conversion of 70.86%. A robust model for predicting monomer conversion that is very suitable for routine industrial usage was obtained. The adequacy of the model was established by ANOVA, normal probability plot and residual Analysis. The synthesized PS sample at optimum conditions was characterized by infra-red spectroscopy, molecular weight and melting point. The results obtained affirmed the good nature of the PS.

Key words: Homo-polymerization, Polystyrene, Response surface methodology, Green Chemistry, Solvent parameters, Kinetics.

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LIST OF ABBREVIATIONS

AA	Acrylic Acid
AIBA	2,2-Azobis (2-ethylpropionamidine)
ANN	Artificial Neural Network
ANOVA	Analysis of Variance
aPS	Atactic Polystyrene
BASF	Badische Anilin-Und Soda-Fabrik
BPO	Benzoyl Peroxide
BPO Blend	Benzoyl Peroxide blend with dicyclohexylphthalate
BuA	Butyl acrylate
BZR	Benzoyloxyl radical
C_I	Concentration of Initiator
C_{I0}	Initial Concentration of Initiator
CCD	Central Composite Design
C_M	Concentration of Monomer
C_{M0}	Initial Concentration of Monomer
C_{R^*}	Radical Concentration
CSTR	Continuous Stirred Tank Reactor
CV	Coefficient of Variation
DADMAC	Dimethyl Ammonium Chloride
DDW	Distilled and De-ionized water (Double distilled water)
DF	Degree of Freedom
D_j	Growing polymer of length j
DMSO	Dimethyl Sulphoxide
DPN	Degree of Polymerization
DTA	Digital Thermal Analyser
EM	Expected Maximization
EtOctNCl	Triethyloctyl Ammonium Chloride
FAME	Fatty Acid Methyl Esters
FRP	Free Radical Polymerization
$g(t)$	Gel effect correlation
GC-MS	Gas Chromatography Mass Spectrometry
HDPE	High Density Polyethylene
HPLC	High performance liquid chromatography

I	Initiator
ILs	Ionic Liquids
I_0	Initial Initiator Concentration
IR	Infra-Red
k_d	Initiator Dissociation Rate Constant
k_{fm}	Chain transfer to monomer
k_{fs}	Chain transfer to solvent
k_p	Propagation Rate Constant
k_{tra}	Chain transfer to chain transfer agent
k_{tim}	Chain transfer to impurity
k_{tin}	Chain transfer to initiator
k_{tp}	Chain transfer to polymer
KPS	Potassium persulfate
KSEs	Kinetics of solvent effects
KT	Kamlet Taft
k_t	Termination Rate Constant
k_{t0}	Terminal Rate Constant at zero monomer conversion
LDPE	Low Density Polyethylene
LSER	Linear solvation energy relationship
M	Monomer
MHS	Mark-Houwink Sakurada
MM	Method of Moment
M_0	Initial Monomer Concentration
MMA	Methyl methacrylate
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
MWD	Molecular Weight Distribution
n-Hexane	Normal Hexane
PA	Polyamide
PC	Polycarbonate
PE	Polyethylene
PF	Phenol formaldehyde
PERP	Project Evaluation and Recognition Programme
PET	Polyethylene terephthalate

PDI	Polydispersity Index
P_i	Growing Polymer of length i
P.I	Polarity Index
PIsoP	Polyisoprene
PolyDADMAC	Polydiallyldimethyl ammonium chloride
PMMA	Polymethyl methacrylate
PP	Polypropylene
PS	Polystyrene
PSO	Pawpaw Seed Oil
PSOB	Pawpaw Seed Oil Biodiesel
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
QSPR	Quantitative structure-property relationships
R	Universal Gas Constant
R^*	Generated radical
R_p	Rate of Polymerization
RPM	Rotation per minutes
RSM	Response Surface Methodology
S	Solvent
SBP	Starch Based Polymer
SDR	Spinning disc reactor
SDS	Sodium dodecyl sulphate
sPS	Syndiotactic polystyrene
SPSS	Statistical Package for Social Scientist
SRC	Styrene radical complex
S_0	Initial solvent concentration
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
THF	Tetrahydrofuran
TNCLDs	Total number chain length distribution
US	United States
WCO	Waste Cooking Oil
WCOB	Waste Cooking Oil Biodiesel

SYMBOLS AND NOTATIONS

b_0	Constant Coefficient
b_i	Linear Coefficient
b_{ii}	Quadratic Coefficient
b_{ij}	Interactive Coefficient
C_p	Specific Heat Capacity ($Jg^{-1}K^{-1}$)
$E_T(30)$	Dimroth-Reichard Electrophilicity Parameter
E_TN	Normalised E_T
f_c	Weight Fraction of Complex Chains
f_f	Weight Fraction of Free Chains
N	Experimental Runs
n^*	Number of Variables
n	Refractive Index
R^2	Coefficient of Determination
t	Time of Flow of Polymer Solution (secs)
t_0	Time of Flow for Solvent (secs)
x	Conversion (%)
X_1	Temperature ($^{\circ}C$)
X_2	Initiator Concentration mol/L
X_3	Reaction Time (mins)
Y	Predicted Response (%)
P_1S^*	Complexed Solvent
ϵ	Dielectric Constant
α	Acidity
β	Basicity
π^*	Dipolarity/Polarizability
λ_k	Live polymer chains
λ_0	Zeroth live Moment
λ_1	First live Moment
λ_2	Second live Moment
μ_k	Dead polymer chains
μ_0	Zeroth dead Moment
μ_1	First dead Moment

μ_2	Second dead Moment
η	Intrinsic viscosity (mL/g)
η_{sp}	Specific viscosity
η_r	Relative viscosity
ΔH_{vap}	Heat of vapourisation (kJ/mol)
C	Carbon
C_8H_8	Styrene
$CHCl_3$	Chloroform
C_6H_6	Benzene
$C_6H_5CH_3$	Toluene
CH_3CN	Acetonitrile
$CH_3COOCH_2CH_3$	Ethyl acetate
CH_3OH	Methanol
$(CH_3)_2SO$	Dimethyl Sulphoxide
Cr	Chromium
Fe	Iron
NaOH	Sodium Hydroxide
Na_2SO_4	Sodium Sulphate
Ni	Nickel

CHAPTER ONE

1.0

INTRODUCTION

1.1. Background of the Study

Polymers are materials with more sterling qualities than other traditional materials. For instance, they have less weight, higher energy efficiency, better performance and durability, and greater flexibility in design and processing (Erdmenger *et al.*, 2009). They constitute an important material for meeting the demands of specialized fields such as engineering, technology and medicine. In the last three decades especially, polymers were not only used as industrial bulk materials but also attracted greater attention in highly specialized fields such as nanotechnology, optics and biomaterials (Bledzki *et al.*, 1981). Each usage requires different specifications of the polymers.

In modern time, there is hardly any sphere of human endeavour (electronics, packaging, construction, automobile, etc) where polymers are not being used in one form or another. The lifestyle of humankind would have been quite miserable without the applications of polymers; infact, polymers form the backbone of the modern society. It is often said that man live in a polymer age (Mishra and Kumar, 2012). Polymerization reactions for the synthesis of polymers are therefore very important chemical processes. Plastic consumption of the world was estimated to be around 200 milion tonnes in 2000 (Rosato *et al.*, 2001). Polyethylene and polystyrene are vinyl based polymers that have found a growing demand and a wide range of applications (Ring, 1999). In this study, polystyrene is the focus of this research because it remains one of the most important and necessary polymers in the polymer processing industry. PS was first produced in 1930 by Dow and BASF in USA (Murat, 2012). It is one of the most widely used thermoplastic in a variety of industrial applications such as packaging, consumer electronics, appliances,

medical devices, toys, inside of car parts and insulating materials among others. After polyethylene (PE), PS is among the most widely produced polymer worldwide (Murat, 2012). In 1996, world production capacity for styrene was near 19.2 million tonnes per year. PS obtained from styrene is one of the most important polymers. In 2011, European production of PS was 3,500 million tonnes (Undri *et al.*, 2014). Quantitatively, in 2001, world production of PS was more than 13 million tonnes with an estimated annual growth rate of 4.5 % (Coastas *et al.*, 2003). Dow Chemical is the world's largest producer with a total capacity of 1.8 million tonnes from facilities across U.S.A, Canada, and Europe (Weissermel, 1997). Asia has been reported to be the overall leader in production and consumption of polystyrene, with 53 % of total world production and 47 % of total consumption of polystyrene in 2010. North America and Western Europe follow distantly at about 17–19 % of the total production and consumption each. Asian consumption of all types of polystyrene is forecast to increase at an average annual rate of slightly over 3 % during 2010–2015. Demand for polystyrene is also driven by China which has the largest electronics and the second largest packaging industry in the world (Research and Market, 2012). Figure 1 shows the global trends in polymer production in the last six decades till recent times while Figure 2 shows the PS end use consumption. PS also finds a special packaging application in food industry as they do not affect odour or taste and are licensed worldwide for contacts with food items. Table 1 shows the PS production on selected country basis.

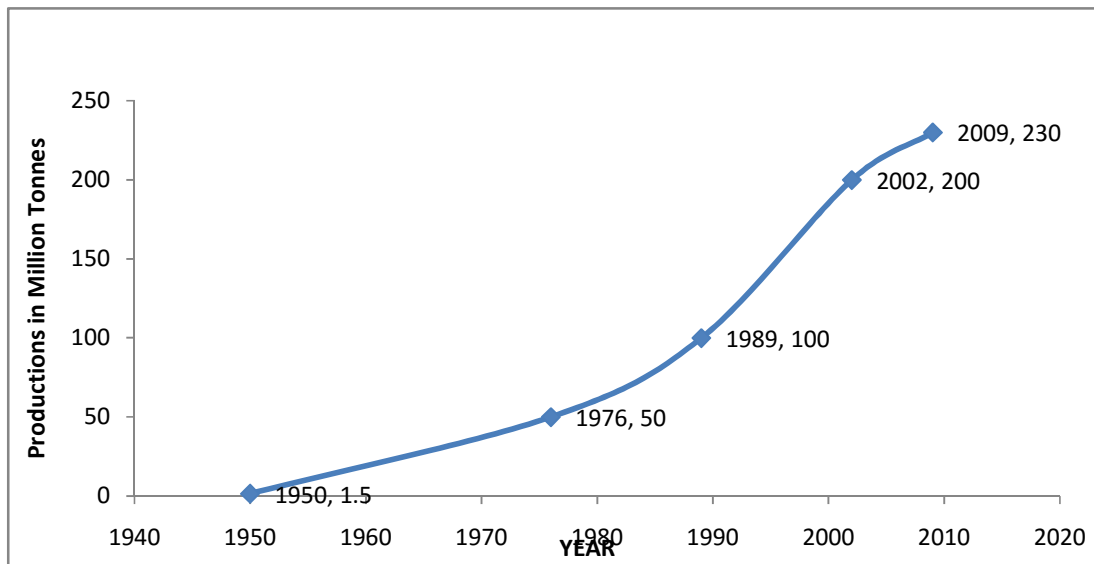


Figure 1: Worldwide productions of polymers, 1950-2009 (Jones *et al.*, 2000)

Table 1: Demography of styrene consumption by country / region (Thousand Tonnes)

USE / COUNTRY	1985	1990	1994	1998
Polystyrene (Canada)	145	183	160	192
Polystyrene (Japan)	1032	1416	1388	1295
Polystyrene (Mexico)	96	126	151	248
Polystyrene (USA)	1844	2271	2657	2876
Polystyrene (Western Europe)	1970	2518	2513	2649
Total	5087	6514	6869	7260

(Ring, 1999)

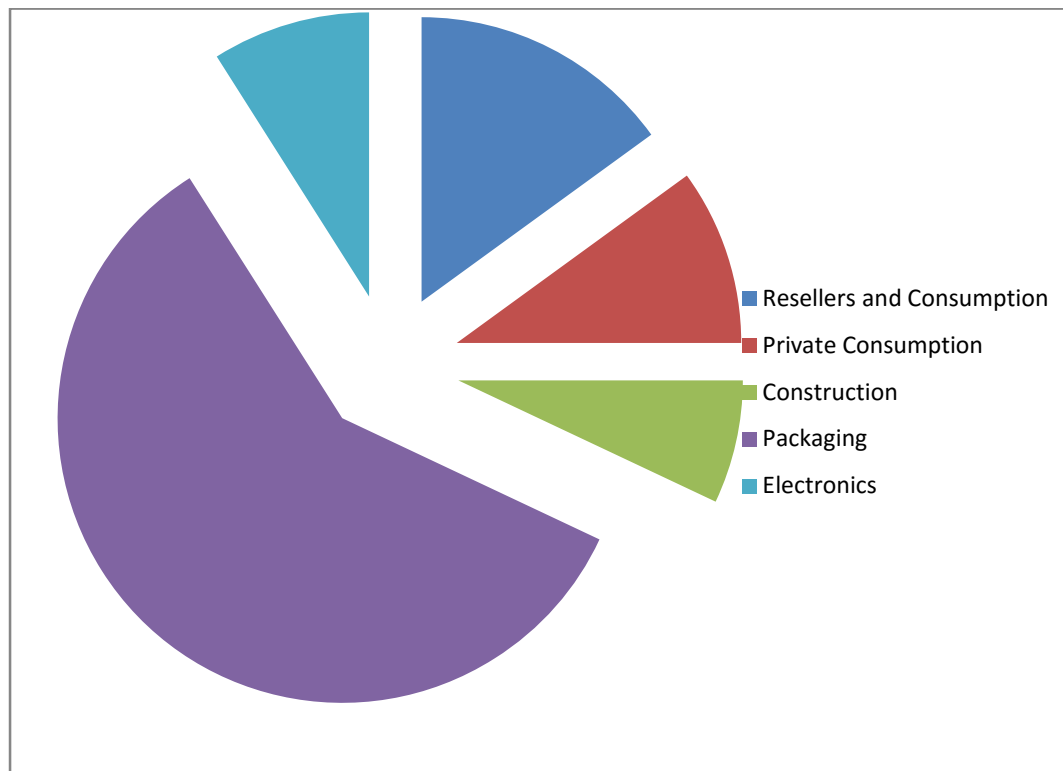


Figure 2: United States polystyrene consumption by end use (PERP Program, 2006)

1.2. Statement of the Problem

Commercially, PS is synthesized by the bulk polymerization process. This production process is prone to the dangerous chemical reaction runaway phenomenon. Solution polymerization has the potential to mitigate this challenge as the introduction of solvent can help dissipate the generated heat. Similarly, the bulk polymerization reactions are associated with increased viscosity, thus impairing uniform mixing for heat and mass transfer. The solvent media again can ameliorate this situation by keeping the viscosity relatively low. While solvents media offer these possibilities, yet their efficiency and dynamics on the polymerization of styrene has not been fully explored. Runaway reactions especially in large scale production have been a dangerous issue for bulk polymerization. This calls for safety concerns, thus a proper reaction method to ensure overall safety is required.

There is also a degree of variation in the performance of solvents during chemical reactions. The evaluation of various solvents to ensure more styrene monomer conversion with ease of product selection without compromising product quality is thus required and lastly, Kinetics models of free radical polymerization are characterized by intricacies, inaccuracies and mathematical rigors which render its routine usage especially in practice a serious challenge. The classical steady state approximation also fails to provide accurate results especially at high conversion owing to increased viscosity of the reaction mixtures. There is therefore the need to develop a more user friendly model suitable for industrial applications.

1.3. Aim and Objectives of the Study

The aim of this work is to rationalize the effects of solvents, develop models (both kinetics and statistical) and optimize Benzoyl peroxide mediated free radical solution polymerization of styrene.

The specific objectives of the study are:

- i. To investigate the compatibility of solvents and initiators in styrene monomer polymerization in a bid to achieve a safe polymerization process coupled with the determination of the link between solvent properties (solvatochromic parameters) and styrene monomer conversion.
- ii. To develop a free radical kinetic model for the prediction of styrene monomer conversion with time of polymerization and to estimate the polydispersity index (PI).
- iii. To carry out optimization studies on styrene polymerization in solvent media using the (RSM) and the development of models in terms of process parameters.

- iv. To investigate the styrene monomer polymerization process using green engineering approach, that is, the use of biodiesel in the polymerization process (Bio – solution polymerization).
- v. To characterize the synthesized polystyrene at optimum conditions (molecular weight / melting point determination, and spectral analysis using Fourier Transform Infra Red Spectroscopy)

1.4. Scope and Delimitation of the Study

The focus of this study is the synthesis of PS in various solvent media, product characterization, process modeling and optimization. After prior solubility, miscibility and compatibility screening of the solvents, the solvent used were limited to acetone, dimethyl sulphoxide, acetonitrile, chloroform, benzene, toluene and ethylacetate. Biodiesel from both waste cooking oil and pawpaw seed oil were used as possible green solvents. The solution viscosity molecular weight approach was adopted for the PS molecular weight determination. Kinetic model for the prediction of styrene monomer with time was developed based on a set of known polymerization reaction elementary steps. The response surface methodology tool was used for the optimization study.

1.5. Significance of the Study

The research has the following significance:

1. No polystyrene plant exists in Nigeria in spite of the large volume of styrene monomer (a petrochemical product) that could be obtained from our refineries. This study will provide basic information useful for the process design and operation of such plant in future.
2. This study will assist in the evaluation of solvents performance in terms of styrene monomer conversion and ease of product separation.
3. The study will offer insight on the suitability of environmental benign solvents for the styrene polymerization in consonance with requirement of green and sustainable chemistry.
4. The study will expand the vista of chemical reaction or engineering knowledge of styrene polymerization especially in terms of the kinetics of the solvents effects (KSEs).
5. The developed free radical kinetic model can be used for the prediction of styrene monomer conversion provided the kinetic parameters are known.
6. The study seeks to provide a user-friendly model suitable for industrial application.

1.6. Definition of Terms

- i. **Analysis of Variance:** This is a statistical technique that is intended to analyze variability in data.
- ii. **Biodiesel:** This product is made through a chemical process which converts oils and fats of natural origin into fatty acid alkyl esters (FAAE).
- iii. **Dead moments:** These are the non active chains.

- iv. **Free Radical Polymerization:** This is a method of polymerization by which a polymer forms by the successive addition of free radical building blocks.
- v. **Green Chemistry:** This is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances.
- vi. **Green Solvents:** They are environmentally friendly solvents or bio-solvents, which are derived from the processing of agricultural crops.
- vii. **Initiation Step:** This describes the step that initially creates a radical species due to influence of initiator.
- viii. **Initiators:** These are substances that can produce radical species under mild conditions and promote radical reactions.
- ix. **Kinetic mechanism:** These are step-by-step descriptions of what occurs on a molecular level in chemical reactions.
- x. **Live moments:** These are the active chains.
- xi. **Micro-structural Analysis:** This shows the arrangement of phases and defect in a sample.
- xii. **Molecular Weight Distribution:** The relative amounts of polymers of different molecular weights that comprise a given specimen of a polymer.
- xiii. **Monomer:** This is any molecule that can be converted to a polymer by combining with other molecules of the same or different types of species. Ethylene is the simplest of all monomers.

- xiv. **Optimization:** This is the scientific method of selecting independent variable combinations that gives optimal objective function from series of possible variable combination. It is usually finding the best way of doing things.
- xv. **Polydispersity:** This is a measure of the heterogeneity of sizes of molecules or particles in a mixture.
- xvi. **Method of Moment:** This is a method of estimation of population parameters.
- xvii. **Polarity:** This is a physical property of compounds which relate to other physical properties, such as melting and boiling points or solubility.
- xviii. **Polymer:** This is a macromolecule formed as a result of combination of several small molecules of the same or different types known as monomers.
- xix. **Polymerization:** This is the chemical combination of two or more molecules of the same or different compounds (monomer) to form larger molecules (polymer). The polymer formed is mostly of high molecular weight.
- xx. **Polymerization Inhibitors:** These are chemicals which stabilize reactive monomers and prevent spontaneous polymerization.
- xxi. **Polystyrene:** Polystyrene is a synthetic aromatic polymer made from the monomer styrene.
- xxii. **Propagation Step:** A free radical reaction mechanism step that has radical reactant(s) and gives radical product(s).
- xxiii. **Response Surface Methodology:** This is the method of using surface graph to model the effect of different independent variables on the objective functions.
- xxiv. **Solvatochromism:** This is the ability of a chemical substance to present different colours due to the change of the solvent in the solution.
- xxv. **Spectral Analysis:** This is the analysis of a spectrum to determine the properties of its source.
- xxvi. **Styrene:** This is an organic compound which serves as monomer for polystyrene.

- xxvii. **Termination Step:** This is the free radical reaction mechanism step that has radical reactant(s) but no radical product(s).
- xxviii. **Trans-esterification:** The process used to convert vegetable oil to Biodiesel.
- xxix. **Trommsdoff Norrish Effect:** This is a dangerous reaction behaviour that can occur in free radical systems. It is due to the localized increases in viscosity of the polymerizing system that slows down the termination reactions.

CHAPTER TWO

2.0

LITERATURE REVIEW

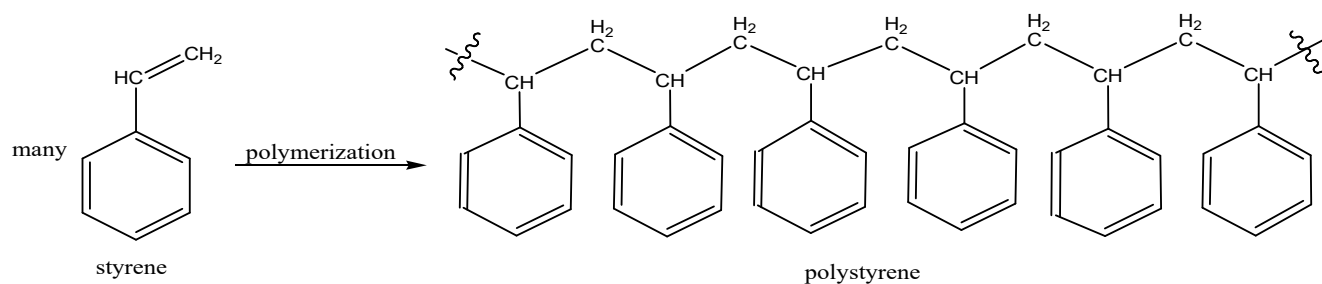
This chapter presents literature reports on styrene monomer and PS polymer and a review of past works on styrene polymerization including details of kinetic modeling and optimization aspects of the chemical process. Further presented review is the detailed mechanism for free radical polymerization, polymerization processes and the techniques for the application of green solvents in polymerization processes. More importantly, the distinctions of the present study from previous reported work have also been articulated.

2.1. Styrene and Polystyrene

A polymer has a large molecular weight. This gives it interesting and useful mechanico-chemical properties. The synthesis of tailor-made polymers with desired molecular design and understanding of the quantitative structure-property relationships (QSPR) have become the main focus area for synthetic polymer/ material Chemists and Engineers. Several authors have reported the synthesis of polymers especially in the last three decades, even till now; the synthesis is experiencing a continuous and growing information trend within the research circle of chemistry, material science, chemical and polymer engineering. This may be due to their wide use as shown in the earlier Figure 2 and their fast replacement over traditional metals.

Ethylene is the simplest form of any vinyl monomer capable of polymerizing. When one of the hydrogen atoms of ethylene is replaced by a phenyl ring, styrene monomer is formed. Styrene is an important aromatic liquid monomer capable of undergoing polymerization reaction under certain conditions. It is commercially manufactured from petroleum to make an aromatic polymer called PS as shown in scheme I. Polystyrene is made up of a long hydrocarbon chain from many styrene molecules. It is one of the most commonly used polymers because of its

recyclable nature and it can be cast into mould. As a colourless polymer, it can be transparent or can be made into any favourable colour.



Scheme I: Polymerization Reaction for the Synthesis of Polystyrene

Table 2: Physico-chemical properties of Styrene

Molecular formula	C ₈ H ₈
Molar mass	104.15 g/mol
Appearance	Colourless
Density	0.909 g/cm ³
Melting Point	-30 °C (243K)
Boiling Point	145 °C (418K)
Solubility in water	<1 %
Viscosity	0.762 cp at 20 °C

(Sigma, 2013)

2.2. Polymerization Processes and Techniques

Different polymerization techniques for the synthesis of PS have been previously reported in the literature: bulk polymerization (O dian, 2004; Stevens,1999; Erdmengeret *et al.*, 2009; Diaconescu *et al.*, 2002; and Joshua, 2001), solution polymerization (Chen *et al.*,1999; Goto and Fukuda, 1999; Ozkam *et al.*,1998, 2009; Altinten *et al.*, 2003, 2006, 2008; Alpbaz *et al.*, 2007; Ghasem *et al.*, 2007, Vicevic *et al.*, 2008; Noor *et al.*, 2010; Novakovic *et al.*, 2003; Hosen and Hussain,

2012; Hosen *et al.*, 2011a, 2011b, 2014a, 2014b; Mohammadi *et al.*, 2014; and Kurochin *et al.*, 2013), emulsion (O dian, 2004; Steven, 1999; Gilbert, 1995), suspension polymerization (O dian, 2004; Steven,1999) and precipitation polymerization (Erdmengeret *al.*, 2009). Details of polymer synthesis techniques as reported by Joshua (2001) are contained in Table 3.

Table 3: Polymerization processes for commercial polymers

S/N	POLYMERS	PROCESSES
1.	Low Density Polyethylene (LDPE)	Bulk
2.	High Density Polyethylene (HDPE)	Solution
3.	Polypropylene (PP)	Solution
4.	Polystyrene (PS)	Bulk
5.	Polycarbonate (PC)	Bulk
6.	Polymethyl methacrylate (PMMA)	Bulk, Suspension
7.	Polyvinylchloride (PVC)	Emulsion, Suspension
8.	polyethylene terephthalate (PET)	Bulk
9.	polyamide (PA)	Bulk
10.	Polyisoprene (PIsoP)	Solution
11.	Starch Based Polymer (SBP)	Emulsion
12.	Phenol formaldehyde (PF)	Solution
13.	Polytetrafluoroethylene (PTFE)	Suspension

(Joshua, 2001)

In contrast to the cracking process of heavy hydrocarbon in the oil refinery industry, styrene polymerization is a building up process with interesting reaction steps (Scheme II-V). The reaction for PS synthesis commences with the generation of radicals through the decomposition of the initiators, followed by the initiation of styrene monomer. The growth of the polymer via the process called propagation, gives the polymer its characteristic high molecular weight. The final step is the (bimolecular) termination reaction in which either (i) two radical species react to form a dead polymer material (ii) disproportionation and (iii) chain transfer processes.

2.2.1. Bulk Polymerization

Odian (2004) in his book (Principles of Polymerization) defined bulk polymerization as the simplest polymerization system which is carried out with the monomer itself but without any addition of diluent or carrier or solvent. Only minute amounts of an initiator are present to initiate the polymerization reaction. The bulk approach however poses some difficulties especially in terms of control of the process if the reaction process is very exothermic. With time, as the polymer builds up, the viscosity of the monomer-polymer solution is increased leading to heat transfer problem (Stevens, 1999). Common commercial uses of bulk vinyl polymerization are in the area of casting formulation and low molecular weight polymers for use as adhesive, plasticizers and lubricant additives. Polystyrene for general purpose is often produced by bulk thermal polymerization in the temperature range from 100 to 200 °C (Arai *et al.*, 1986).

2.2.2. Solution Polymerization

In solution polymerization, the tradition is to introduce solvents to aid in efficient heat transfer facilitatory processes, dissolution of the monomers and polymer (Stevens, 1999). Solution polymerization has the potential to mitigate the challenge faced by bulk polymerization as the solvent can help dissipate the heat generated. Also, polymerization reactions are associated with increased viscosity, thus impairing uniform mixing for heat and mass transfer. The solvent media in solution polymerization can ameliorate this situation by keeping the viscosity relatively low as was observed by Gonzalez *et al.*, (2007). In addition, solution polymerization is more amenable to laboratory study and has continued to attract research attention. It also holds the promise of enabling process intensification for large scale production of polystyrene. The two main desires of a polymerization process are to maximize productivity and improve quality of polymer products. The former is reflected by the monomer conversion while the latter is encapsulated in

the macromolecular architecture (number average molecular weight, weight average molecular weight, and polydispersity index). Both conversion and macromolecular architecture are influenced by the reaction conditions (Hosen *et al.*, 2011a; 2011b; 2014a; 2014b; Vasco de Toledo *et al.*, 2005; Gharaghani *et al.*, 2012). In solution polymerization, the reaction conditions should include solvent type and solvent-initiator compatibility. This fact seems lost on previous research efforts. This is evident in most of the reported literature on various aspects of solution polymerization of styrene as toluene is the common solvent used (Goto and Fukuda, 1999; Ozkam *et al.*, 1998; 2009; Altinten *et al.*, 2003; 2006; 2008; Alpbaz *et al.*, 2007; Ghasem *et al.*, 2007; Vicevic *et al.*, 2008; Noor *et al.*, 2010; Novakovic *et al.*, 2003; Hosen and Hussein, 2012; Hosen *et al.*, 2011a; 2011b; 2014a; 2014b; Mohammadi *et al.*, 2014). There are, however, some reports in the literature where other solvents are used in styrene polymerization to achieve specific ends. For example, Kurochkin *et al.*, (2013) used o-xylene as solvent in their investigation of oxidative polymerization of styrene in the presence of molecular oxygen to regulate the length of polymer chain. To this end, the authors also alluded to the effectiveness of solvents containing aliphatic groups such as toluene, butyl acetate, acetone, etc. In another recent study, Bahring *et al.*, (2014) used solvents of different polarities, namely 1,2 dichloroethane, methylcyclohexane, and trichloromethane, to regulate the degree of polymerization of weakly associated supramolecular oligomers. However, extra care must be taken in the choice of solvent since it will have a serious impact on the chain transfer reaction, otherwise it can limit the molecular weight (Oodian, 2004). One limitation of this process is the difficulty in removing the solvent completely from the finished polymer and of course, the environmental concerns associated with the organic solvents (Stevens, 1999). In the present study, batch solution polymerization of styrene was carried out using seven different solvents, namely acetone,

chloroform, benzene, toluene, acetonitrile, ethyl acetate, and dimethyl sulphoxide (DMSO), and different initiators i.e benzoyl peroxide (BPO) and benzoyl peroxide blend with dicyclohexylphthalate (BPO blend). Solvent effects were determined in understanding the influence of polarity on the conversion of styrene through correlation with Kamlet Taft (KT) parameters in a linear solvation energy relationship (LSER). The choice of ideal solvent for styrene polymerization was then made based on monomer conversion and ease of solvent separation.

2.2.3. Emulsion Polymerization

Water rather than organic solvent is basically used as efficient heat transfer medium during emulsion polymerization process (Oadian, 2004; Stevens, 1999). Monomer in emulsion polymerization is dispersed in the continuous aqueous phase by an emulsifier. Water soluble initiator is then added to the process to generate the primary free radicals which then diffuses into micelles swollen with monomer molecules. As monomer is used up during the polymerization reaction, more monomers enter the micelles to continue the reaction. Termination step by radical combination occurs when a new radical diffuses into the micelles. High molecular weight polymers are achievable during this process because only one radical is present in the micelles due to termination reaction (Gilbert, 1995). The entire process is very complex, with the heterogeneous phase of the process and also the reaction kinetics becomes significantly different from both bulk and solution polymerization.

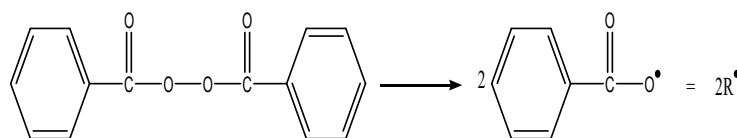
2.2.4. Suspension Polymerization

Water also serves as polymerization medium in suspension polymerization but most times, not always miscible with the monomer. The process involves mechanically dispersing the monomer in the non-compatible liquid - water (Oadian, 2004; Stevens, 1999). An Initiator that is soluble in

the monomer is used for the polymerization process to occur. Monomer is kept in suspension by continuous agitation and the use of stabilizers such as polyvinylalcohol or methylcellulose. Polymer product obtained from this process are often in the form of granular beads if the process is carefully controlled (O dian, 2004). This polymer is easy to be handled and can be isolated by filtration or by spraying using spray dryer into a heated chamber (Stevens, 1999). Suspension polymerization also allows efficient heat transfer and therefore the reaction is easily controlled. However, Tina *et al.*, (2010), reported that an alternative approach to produce PS in a simple way is by precipitation polymerization. The advantage of this method is the absence of the very expensive stabilizers and the difficult requirement to remove the stabilizers in comparison to heterogeneous polymerization technique such as emulsion and suspension polymerization.

2.3 Reaction Scheme for Styrene Polymerization

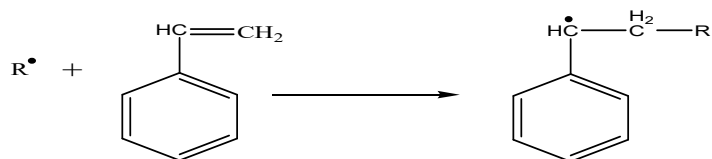
Decomposition of Initiator:



(II)

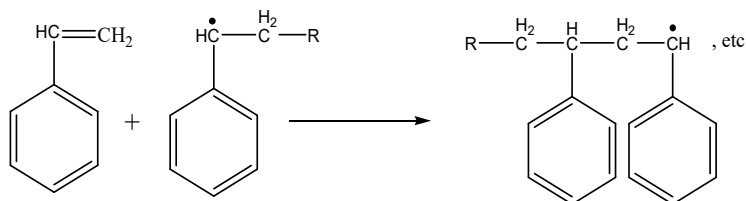
Benzoyl Peroxide

Benzoyloxy radical (BZR)

Initiation:

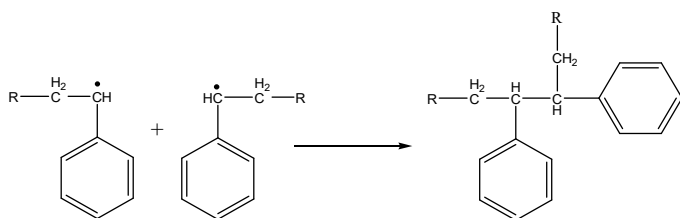
(III)

BZR Styrene Styrene radical complex (SRC)

Propagation:

(IV)

Styrene SRC Styrene Polymer Radical (SPR)

Termination Step:

(V)

SRC SRC Dead Polymer

The process industries generally comes with its challenges such as safety issues, energy utilization, use of hazardous chemicals and others. Polymerization reaction for instance is known to be the most frequent cause of thermal run away incidents in industrial chemical processes

(Plates 1-6 and Table 4). Cherbanski *et al.*, (2007) and Vijayaraghavan *et al.*, (2004) both observed that explosions due to thermal runaway are one of the major safety issues faced by chemical process industry. Tseng and Lin (2011) in their detailed study affirmed that runaway reactions can either be induced by hot spots or caused by insufficient heat removal. The extent and severity of its occurrence is however dependent on the polymerization technique employed. The bulk approach for PS synthesis is however fraught with the challenge of heat transfer and mixing which become difficult as the viscosity of reaction mixture increases. Continuous mixing of the reacting mixtures requires extra large mechanical power which is on a debit side in terms of cost. The difficulty in mixing also increases the pumping power of the reacting vessel. This is compounded by the highly exothermic nature of free radical addition polymerization (Oadian, 2004). All these lead to auto-acceleration, a situation that occurs when the heat produced by polymerization does not dissipate quickly enough. The surplus heat raises the temperature of the reaction mass, which causes the rate of reaction to increase. This in turn accelerates the rate of heat generation. As the heat builds up, the reaction vessel may be at risk from over-pressurisation due to violent boiling. The polymerization process accelerates beyond safe control, a situation called thermal runaway reaction (Joshua, 2001). This is detrimental to the safety, maintenance and plant operations. The situation was exactly what took place in 1966 in New York where a polystyrene plant got ablaze claiming 11 lives and lots of properties as reported by Willey (2000) (Plates 1-6). A similar incident occurred in Taiwan in 2001, where an aryllic reactor was overheated leading to reaction runaway. The released materials formed a vapour cloud and exploded which caused 1 dead, 112 injured and 46 nearby plants damaged (Ho *et al.*, 1998). The reactor was overheated causing a run away reaction. The total loss was estimated to be 10 million US dollars (Kao, 2002). Relatively recent related accidents are as

shown in Table 4. A thorough knowledge of exothermic reactions in polymerization system is essential at this point. This is not only to help in mitigating disastrous events such as catastrophic fires and explosions but also in providing the means for designing in – built safety system and assessing thermal sensitivity or reaction mixtures and products.



Plate 1: Industrial estate in New York housing the polystyrene plant (Willey, 2000)

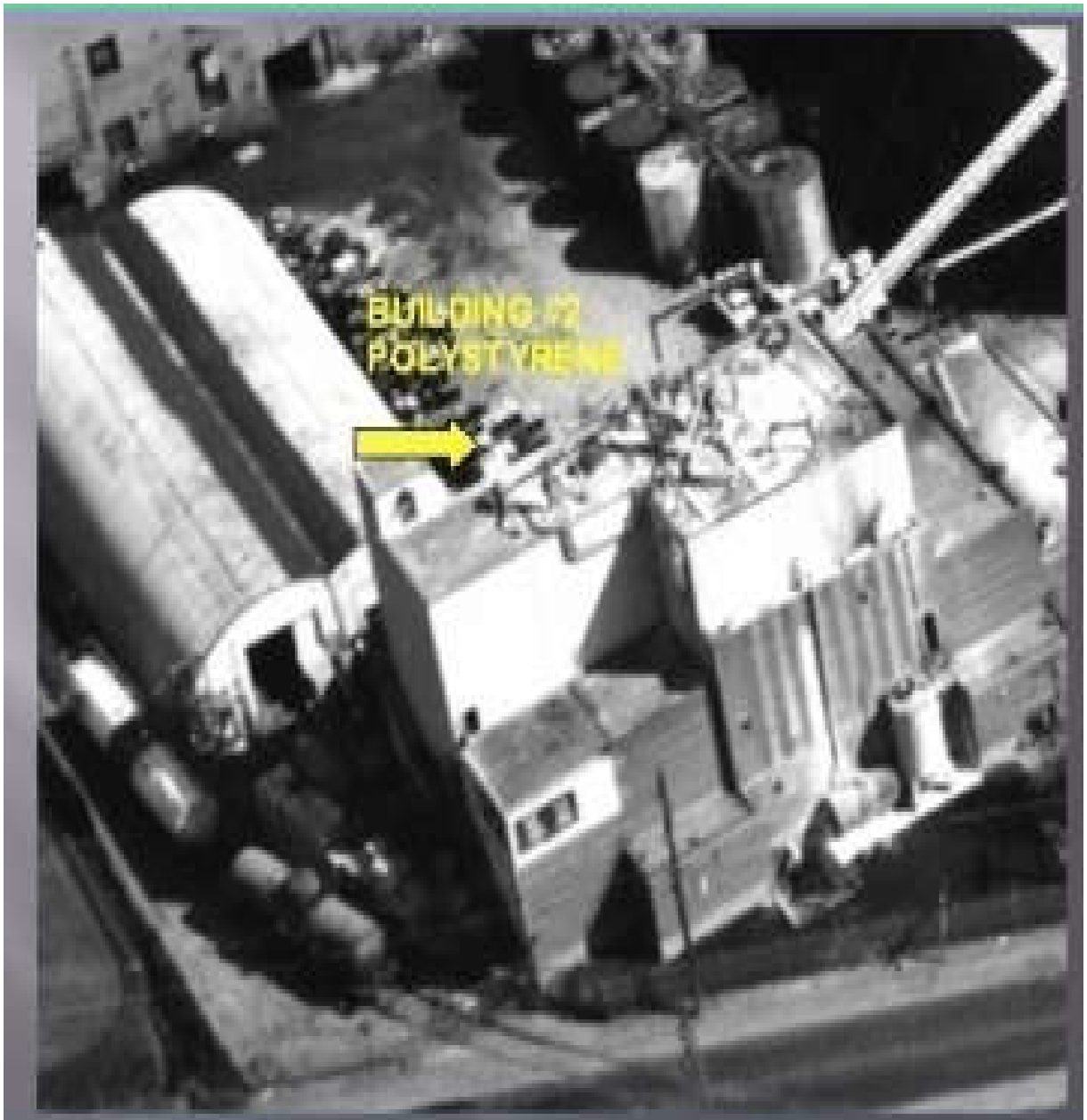


Plate 2: Polystyrene plant (Willey, 2000)



Plate 3: Inferno at the polystyrene plant [Accident occurred on October 13, 1966 in New York] (Willey, 2000)



Plate 4: Inferno at the polystyrene plant [Accident occurred on October 13, 1966 in New York] (Willey, 2000)



Plate 5: Remnant of the Polystyrene plant after the inferno [Accident occurred on October 13, 1966 in New York] (Willey, 2000)



Plate 6: Remnants of the Polystyrene plant after the inferno [Accident occurred on October 13, 1966 in New York] (Willey, 2000)

2.4 Styrene to Polystyrene Batch Process

The polymerization process steps as carried out on the New York PS plant by the PS manufacturer involved

- Loading the reactor with styrene
- Addition of polymerization Catalyst
- Heating the reactor to 95 °C
- Holding for 2 to 8 hours

Typical Bulk
Polymerization
Approach

One solution to this problem is the introduction of a good solvent to reduce the viscosity of the reacting mixture. This translates into improved heat transfer and the prevention of thermal runaway of the reaction by absorbing the heat of polymerization thus increasing the heat capacity of the system. Though the problem with solvent is the inefficiency associated with their recovery and reuse, a separate solvent removal and recovery unit could be introduced into the existing process design (Figures 3 and 4). There is therefore a strong need to search for suitable solvents with high performance in terms of monomer conversion, ease of product separation and meeting the requirement of green and sustainable chemistry.

Table 4: Selected accidents related to styrene/benzoyl peroxide initiator and its derivatives

Date	Location	Fatalities	Injuries	Hazard
07/05/1994	Kaoshiung , Taiwan	1	0	Explosion
23/06/1999	Pasadena , Texas, USA	2	4	Explosion
25/07/1999	Hong Kong , China	0	0	Explosion
06/10/1999	Chiayi , Taiwan	0	1	Explosion
27/03/2000	Pasadena , Texas, USA	1	71	Explosion
12/03/2003	Yechon , South Korea	1	0	Explosion
May, 1990 ¹	Japan (BPO)	17	9	Explosion
June, 1993 ¹	China (BPO)	33	27	Explosion
May, 2001 ¹	Taiwan (BPO)	121	1	Explosion
January, 2003 ¹	USA (BPO)	1	0	Explosion

(US Chemical Safety and Hazard Investigation Board)¹ (Liao *et al.*, (2013))

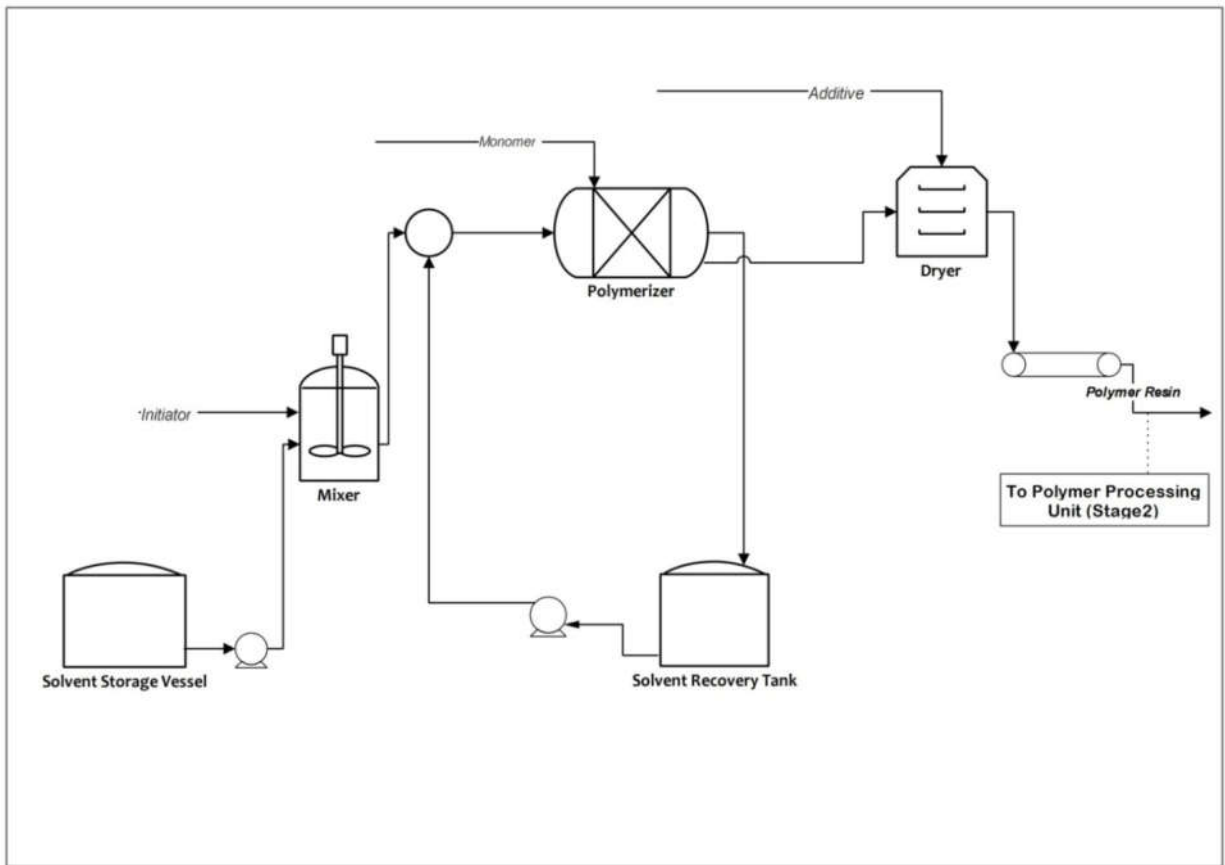


Figure 3: Process flow diagram for solution polymerization of styrene (Stage 1)

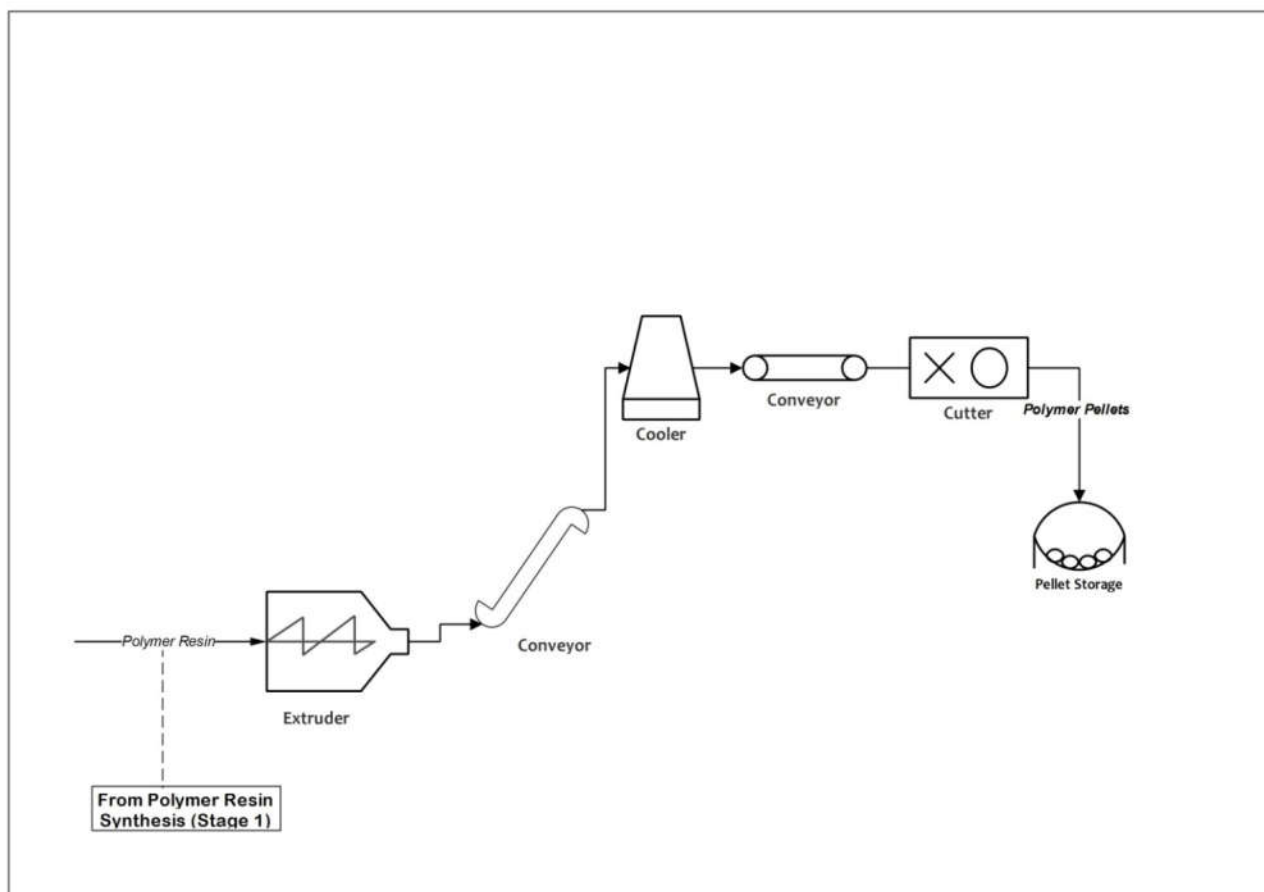


Figure 4: Process flow diagram for solution polymerization of styrene (Stage 2)

The 1966 NY Polystyrene explosion situation may have been averted if reaction conditions such as solvent use and type, solvent-monomer ratio and solvent-initiator compatibility have been considered. These facts seem lost in previous research efforts. Table 5 provides a comprehensive list of solvent mediated polymerization.

Inspite of the large volume of research, agreement is yet to be reached on the nature of solvent effects and the extent of its influence, as literature information reveals lack of acceptable generalization of findings especially for styrene polymerization reactions.

Table 5: Solvents for some vinyl monomers polymerization

S/N	Polymerized monomer	Solvents used	Reference
1.	Methyl methacrylate	Benzyl alcohol	O'Driscoll <i>et al.</i> , (1997)
2.	Methyl methacrylate	Toluene, Tetralin, Tetrahydrofuran (THF) methyl isobutyrate, Phenyl isobutyrate	Beuermann <i>et al.</i> , (2004)
3.	Methyl methacrylate	Toluene, Benzonitrile	Fernandez-Garcia <i>et al.</i> , (1998)
4.	Ethylene	Toluene, Tetrahydrofuran (THF)	Etienne <i>et al.</i> , (2009)
5.	Styrene	Toluene	Goto and Fukuda (1999); Ozkan <i>et al.</i> , (1998; 2009); Altinten <i>et al.</i> , (2003; 2006; 2008); Alpbaz <i>et al.</i> , (2007); Ghasem <i>et al.</i> , (2007); Vicevic <i>et al.</i> , (2008); Noor <i>et al.</i> , (2010); Novakovic <i>et al.</i> , (2003); Hosen and Hussain (2012; Hosen <i>et al.</i> , (2011a; 2011b; 2014a; 2014b); Mohammedi <i>et al.</i> , (2014)
6.	Styrene	Ethyl benzene	Mermier <i>et al.</i> , (2015)
7.	Isobornyl methacrylate	Toluene, Tetralin, THF, Methyl isobutyrate, Phenyl isobutyrate	Beuermann <i>et al.</i> , (2004)
8.	Acrylonitrile	Dimethyl sulphoxide, Tertiary butyl alcohol	Lyoo <i>et al.</i> , (1999)
9.	Vinyl acetate	Ethyl alcohol	Kumbhare (2014)

Typical polymerization processes employed industrially till date are bulk polymerization, solution polymerization, emulsion polymerization and suspension polymerization, Stevens (1999) and Odian (2004). However, for the case of styrene, bulk and suspension polymerization processes find much industrial application (Erdmenger *et al.*, 2009; Diaconescu *et al.*, 2002; Joshua, 2001; and Chen *et al.*, 1999; Arai *et al.*, 1986). Each of these polymerization processes and techniques has some merits and limitations. These polymerization processes can either be homo-polymerization, co-polymerization, ter-polymerization, or even tetra-polymerization. Various additives can be introduced into the reaction system which could take place in batch, continuous or tubular reactors to obtain polymer of better end use properties. Different

exogeneous parameters such as temperature, initiator concentration, reaction time, flow rate, etc control the desired end properties of the products. In this study however, styrene polymerization was carried out in a batch laboratory reactor to ensure a much convenient operation for its parametric studies.

2.5 Kinetics of Free Radical Polymerization

Considerable percentage of unsaturated monomers capable of undergoing polymerization reactions comes from the petrochemical industry. Most of these compounds by their chemistry can react with free radicals. For this reason, free radical polymerization (FRP) remains a commonly used route for the synthesis of functionalized polymers. In addition, the insensitivity of FRP to impurities, the moderate operating conditions involved and multiple polymerization reaction techniques associated with FRP has encouraged their use till date (Mastan *et al.*, 2015), especially in the synthesis of high molecular weight polymers (Krzysztof, 1998). Though, there are reports about the limitations of FRP in terms of poor control of molecular weight, molecular weight distribution and difficulty of synthesizing well defined co-polymers and polymers with a pre-determined functionality (Mishra and Kumar, 2012). Nonetheless, FRP still finds wide applications in paints, safety glasses, and other polymer industries including synthesis of latexes, plexiglass, and foamed polystyrene, high molecular weight methyl methacrylate respectively.

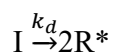
Polymerization reactions either by addition or condensation strategies irrespective of the modes of initiation have created a lot of unsolved and complex reaction problems (Tobita and Zhu, 2014). A problem associated with the reaction is a unique and unified set of elementary steps for free radical vinyl monomer polymerization which are still been debated. Interestingly, there is strong evidence from the body of open literature of the continuous and intensive research on the reaction from polymer engineering /polymer scientist and material chemistry research

groups. From the report of lengthy list of researchers such as; Almeida *et al.*, (2008), Kiparissides *et al.*, (2006), Mohammed *et al.*, (2011), Chen (2000), Zhu *et al.*, (2001), Pladis and Kiparissides (1998), Achilias and Kiparissides (1992), Penlidis *et al.*, (1992), Kee and Yhu (1988), Ogo (1984), Goto *et al.*, (1981), Wu *et al.*, (1982), Yamamoto and Sugimoto (1979), Friis and Hamielec (1976), Hui and Hamielec (1972), Ehrich and Mortimer (1970), Osakada and Fan (1970), and Hamielec and Hodgins (1967), a basic free radical styrene polymerization chain process /mechanism has three essential reaction steps namely:

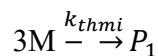
- Initiation (Radical generation /Activation)
- Propagation (Chain growth)
- Termination (Chain Cessation)

2.5.1 Initiation

The case during the initiation is the homolytic dissociation of the initiator to form a pair of radicals. This step is considered to be a two stage process as described by Mohammed *et al.*, (2011). As earlier stated, the homolytic dissociation of the initiator for radical generation is the first while the addition of the generated radical to the first monomer molecule to produce the initial chain carrying radical is the second initiation stage.



Hui and Hamielec (1972) proposed a thermal initiation mechanism which is represented by third order kinetics with respect to the styrene monomer.

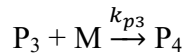
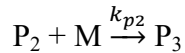
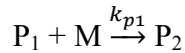


In support of the Hui and Hamielec (1972) thermal initiation proposal, Buback (1980) studied the thermally initiated polymerization of ethylene where it was similarly observed a very slow

thermally initiated reaction resulting in high molecular weight polymers at temperatures 180-250 °C and pressures up to 2500 bars.

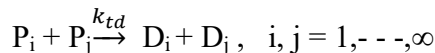
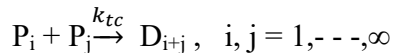
2.5.2. Propagation

Mass consumption of monomer molecules (about 6.02×10^{23} molecules in 1 mole of monomer) by successive additions to form a large growing polymer chain takes place at this stage of chain propagation reaction:



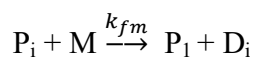
2.5.3 Termination

Termination takes place either by radical re-combination with rate constant k_{tc} to form a single polymer molecule or by disproportionation with rate constant k_{td} which yields two separate polymer molecules.

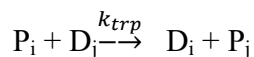


Termination by disproportionation is negligible in the case of styrene polymerization (Chen, 2000). Aside the aforementioned, the following side reactions to terminate the radical species simultaneously takes place in most vinyl monomer polymerization.

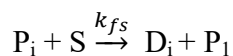
Chain Transfer to Monomer



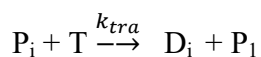
Chain Transfer to Polymer



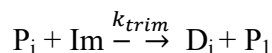
Chain Transfer to Solvent



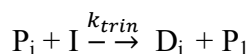
Chain Transfer to Transfer Agent



Chain Transfer to Impurity



Chain Transfer to Initiator



2.6 Previous Study on vinyl Monomer Polymerization and Kinetic Modeling of FRP

The polymerization reaction commences with the generation of initiator radicals, followed by the initiation of monomers. The growth of the polymer via the process called propagation, gives the polymer its characteristic high molecular weight. The final step is the bimolecular termination reaction in which two radical species react to form a ‘dead’ polymer material. It is important to realize that these reactions take place simultaneously to varying degrees during the polymerization process. As a result, the end-product does not consist of polymer chains with one unique size, instead, the polymer consists of a distribution of polymer chains with a variety of different sizes (Willemse, 2005).

Hui and Hamilec (1972) similarly reported that purified styrene can undergo thermal polymerization at a reproducible rate of about 0.1 % per hour at 60 °C, 2 % per hour at 100 °C

and 16 % percent per hour at 130 °C. Formation of low molecular weight oligomers and the close control of the polymerization temperature are observed to be disadvantages of the thermal polymerization process. Tefera *et al.*, (1994) also investigated both experimentally and theoretically, the free-radical suspension polymerization of styrene at different temperatures (i.e. 70, 75, and 80 °C) respectively and initiator concentrations (i.e., AIBN: 0.15–0.45 wt.% of styrene). Devonport *et al.*, (1997) studied the thermal initiation of styrene in the presence of 2, 2, 6, 6-Tetramethyl-1-piperidinyloxy (TEMPO) at 125 °C. They showed that low polydispersities and controlled molecular weights could be achieved under these conditions, although the degree of control was not as good as for unimolecular or bimolecular initiating systems. Malkin and Kulichikin (1985) used a series of alkyl methacrylates and styrene with benzoyl peroxide initiator to study the rheo-kinetics of polymer system. The research focused on the effects of initial concentration of initiator, reaction temperature, and reaction time on the viscosity of the polymer system. From the reports of researchers (Teferal *et al.*, 1994; Devonport *et al.*, 1997; Michael *et al.*, 1997), styrene is polymerized by cationic, anionic, Ziegler-Natta and free radical methods. In recent years, McHale *et al.*, (2007) intensified research on styrene polymerization using supercritical CO₂ as a green solvent. Michael *et al.*, (1997) studied the effect of free radical propagation rate coefficients of both methyl methacrylate (MMA) and styrene using Pulsed-Laser polymerization. The data reported in their article strongly supports the existence of either a radical-solvent or radical-monomer complex participating in the propagation reaction by modifying the reactivity of the reactants. Rasul *et al.*, (2008) successfully investigated the performance of base catalysts (MgO, BaO, and CaO) on the degradation of polystyrene to styrene monomer where special focus was placed on mixing the catalyst with polystyrene particles in a reactor to increase the rate of degradation. Quantity of styrene obtained from such

study and its easy polymerizability to obtain PS of appropriate molecular architecture are areas yet to be explored. Cunha *et al.*, (2013) were able to analyze the influence of parameters such as agitation speed and initiator concentration on the final properties of high impact PS. The study affirmed that the PDI strongly depend on initiator concentration.

Frounchi *et al.*, (2002) developed a model by modifying the assumptions made in the Marten-Hamielec and Vivaldo-Lima model of 1994 to achieve a better conversion prediction especially at high conversion. Coastas *et al.*, (2003) developed a kinetic model capable of predicting the evolution of polymerization rate . The free volume model was employed to account for diffusion controlled, termination, and propagation and initiation reaction. Maafa *et al.*, (2007) proposed a dynamic Monte Carlo model for bifunctional initiators. The results of their model compared well with the method of moment when applied to the polymerization of styrene. The production of polymers with desired end-use properties is of significant financial importance to the polymer industry. One of the most important molecular properties that control the end-use characteristics of polymers is the molecular weight distribution (MWD) as it directly affects the physical, mechanical and rheological properties of the final product (Veros, 2003). The MWD of a polymer can be characterized by the number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity (PDI). (MWD)/Polydispersity index (PDI) are considered as a fundamental property that determines polymer properties and hence its applications. The development of kinetic model for the estimation of polystyrene polydispersity is a tasky component of polymerization research. Knowledge of the rate coefficients of all fundamental steps in a free-radical polymerization process is of much importance as these are invariably related to the structure and therefore to the properties of the polymer. Experimental determination of the important property i.e. Polydispersity index (PDI), is not only tasking and

time consuming but also very expensive. It is on a strong debit side in terms of cost in the polymer industry. Molecular weight distributions are determined by using the HP 1090 HPLC system, equipped with the HP 1047A RI (refractive index) detector and a four-column set configuration (10^5 , 10^4 , 10^3 , 10^2 Å 30 cm x 7.8 mm microstyragel columns) (Suryaman, 2006). The purpose of constructing a detailed kinetic model is to be able to correlate the reaction conditions (e.g. temperature, initiator concentration, reaction time, etc) with the polymer quality (e.g. Molecular Weight Distribution). This attempt has been seldomly reported until recent times, nonetheless, details of modeling technique for the estimation of PDI that have found wide acceptance and those that were recently proposed can be found in Willemse (2005). Garg *et al.*, (2014) developed an analytical method of solving polymer kinetic model that predicts much better than previous numerical solution. Their method herein referred to as Garg approach is used extensively in this work rather than numerical solution. Earlier researchers such as Baillagou and Song (1985), Louie *et al.*, (1985) and Frounchi *et al.*, (2002) have used various versions of reaction mechanism and recorded varied success by comparing the numerical solution with experimental results. Side reactions have been limited to chain transfer to monomer and solvents in order to reduce the increased level of complexity in the analytical solution of the kinetic model. This side reaction limitation made our reaction scheme similar to that of Garg *et al.*, (2014) except where they introduced transfer to chain transfer agent. As earlier mentioned, the Garg approach utilizes the method of moment analysis in the modeling approach. The same method has been found successful in predicting statistically averaged properties of polymers (Dhib and Al-Nidawy, 2002, Kiparissdes *et al.*, 2006, and Zhu *et al.*, 2001). The method of moments transforms the original high-dimensional systems of differential equations into a low-order system of equations by introducing the leading moments of the distributions of interest.

The major limitation of models based on the method of moments is that they only track average quantities. While adequate for most situations, the MM cannot examine, for example, the combined effects of chain-scission and long-chain branching on the polymer architecture, or to incorporate chain-length-dependent termination kinetics into the kinetic scheme (Konstadinidis, 1992, Achilias and Kiparissides *et al.*, 1992). Summarily, the first phase of the kinetics aspect of study is to carry out a mass balance of all the chemical species present, derive an improved kinetic model for the styrene monomer conversion prediction and apply the Garg approach for the determination of polymer PDI.

Furthermore, kinetic models of the free radical polymerization are characterized by intricacies, inaccuracies and mathematical rigors which render its routine usage especially in practice a serious challenge. The common classical steady state approximation also fails to provide accurate results especially at high conversions owing to increased viscosity of the reaction mixtures. This is further compounded by increased temperature for this inherently exothermic reaction particularly when carried out without adequate heat removal. All these stimulated phenomena such as gel, glass and cage effect which complicates kinetic modeling. Several workers have attempted incorporating each of these occurrences in their models to varying degree of success (Achilias and Kiparissides, 1988; Venkateshwaran and Kumar, 1992; Achilias and Kiparissides, 1992; Frounchi *et al.*, 2002; Keramopoulos and Kiparissides, 2002; Keramopoulos and Kiparissides, 2003; Achilias, 2007; Verros and Achilias, 2009). More recent is the work of Garg *et al.*, (2014). They derived an analytical solution for the free radical polymerization and validated same for various possible scenarios to establish its general applicability. Another recent effort by Yong *et al.*, (2015) to model free radical polymerization using dissipative particle dynamics hardly addressed the enumerated shortcomings. All these

efforts largely result in models with limited range of application. There is therefore the need for a robust model that is valid for all range of conversions and yet simple enough for routine industrial application. Such model should be based on process parameters rather than live and dead chains as obtained in the classical kinetic models. To this end, RSM adopted herein proves invaluable over the classical kinetic models. Literature is scarce on the deployment of this methodology in the study of solution polymerization of styrene with the view to elucidating the single and interactive effect of process variables on polymer architecture, obtain a suitable model and optimization of such variables.

2.7 Green Polymerization Reaction Engineering

Bulk polymerization processing approach is highly exothermic with increasing viscosity therefore making agitation of the reacting mixtures increasingly difficult. The use of solvents as part of the reaction mixture has been reported earlier to ameliorate the problem of increasing viscosity during polymerization (Kehinde *et al.*, 2013). Gani *et al.*, (2005) have also identified the roles played by solvents in various chemical reactions, few of which are;

- i. They are media that bring reactants together.
- ii. They act as reactants to react with a solute when it cannot be dissolved.
- iii. They act as carriers to deliver chemical compounds in solutions to their point of use in the required amount.
- iv. They act as heat transfer medium.
- v. Gas phase reactions which are normally at high temperatures and or pressures, could be performed in the liquid phase under significantly lower temperatures and or pressures.

In spite of the extensive range of research on the use of solvents during polymerization, solvents are still not considered favourably for chemical reactions. For instance, Gani *et al.*, (2005) claimed that solvents present numerous environmental, health and safety challenges including

human and eco-toxicity, possess safety hazards and waste management issues. In as much as solventless reactions are rare and there is also a strong and recent campaign for sustainable chemistry (Tables 6 and 7), giving rise to the interplay of two opposing forces, there is therefore the need to create a balance in terms of minimization and optimization of the use of solvents to enhance minimum environmental and operational concerns.

Table 6: Toxicity of some organic polymerization solvents

Solvents	Toxicity
Toluene ¹	Narcotic, Liver and Kidney damage at high concentration
Benzene ¹	Carcinogenic
Ethylbenzene ¹	Carcinogenic
Ethylacetate ¹	Narcotic, Liver and Kidney damage at high concentration
Xylene ¹	Narcotic at high concentration
Biodiesel ²	Non-Hazardous material.

1: (Budavari *et al.*, 1989) 2: (Mittelbach and Remschmidt, 2004)

Table 7: Solvent selection guide

Preffered	Usable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Toluene	Hexane
Ethanol	Methylcyclohexane	Di-isopropylether
2-Propanol	tertiary Butyl methyl ether	Di-ethylether
1-Propanol	Isooctane	Dichloromethane
Heptane	Acetonitrile	Dichloroethane
Ethyl acetate	2-Methyltetrahydrofuran	Chloroform
Isopropyl acetate	Tetrahydrofuran	N-Methyl-2-pyrrolidone
Methanol	Xylenes	Dimethylformamide
Methyl ethyl ketone	Dimethylsulfoxide	Pyridine
1-Butanol	Acetic Acid	Dimethylacetamide
t-Butanol	Ethylene Glycol	Dioxane
		Dimethyloxtethane
		Benzene
		CarbonTetrachloride

Sheldon 2012) and Dunn (2011)

Therefore, rather than altering the polymerization technology, one could look for more environmentally friendly solvents to replace more harmful conventional solvents. According to Singh *et al.*, (2000), new options to generate polystyrene using more environmentally compatible approaches that reduce the need for heavy metal and catalysts that could be carried out at ambient or near ambient temperatures, that would require less specialty equipment, or the use of catalysts derived from renewable resources could offer a useful alternative to the more traditional synthetic methods. Diversity in function of enzymes under mild reaction conditions has prompted interest in enzyme-based polymerizations (Gross *et al.*, 1998; Zaks and Kibanov, 1985; Keys *et al.*, 1988; Chaudhary *et al.*, 1995; and Faber and Franssen, 1993). Enzymatic oxidative free-radical polymerizations of phenols or anilines have been extensively studied almost at the same time by Dordick *et al.*, (1987), Akkara *et al.*, (1991), Rao *et al.*, (1993) and Ayyagari *et al.*, (1995). Furthermore, peroxidase reactions have been extended to acrylamide with the addition of a α -diketone to function as an enzyme substrate and initiator for polymerization (Emery *et al.*, 1997 and Teixeira *et al.*, 1999). Alternative solvents suitable for green chemistry are those that have low toxicity and are easy to recycle, are inert and do not contaminate the product. There is no perfect green solvent that can apply to all situations and therefore decisions have to be made on the suitability of a green solvent for a particular reaction. Numerous chemical engineers, chemists, macromolecular and material scientists have examined the homo-polymerization of vinyl monomers such as ethylene, styrene, methylmethacrylate, vinyl acetate, etc in aqueous media (Emulsion Polymerization). It is estimated that 40-50 % of free radical polymerization is conducted by emulsion polymerization (Gilbert, 1995). The use of water as the dispersion medium is environmentally friendly compared to using volatile organic solvents and also allows excellent heat dissipation during the course of the polymerization. Etienne *et al.*, (2009)

performed free radical polymerization of ethylene in water from a water soluble initiator 2, 2-azobis (2-amidinopropane) dihydrochloride) where stable polyethylene latex were obtained though the authors claimed that the polymerization process was not a standard one. Li and Brooks (1993) developed a model for simulating the semi-batch emulsion polymerization of styrene where polymer seed particles were introduced initially in the reaction. The model was used to calculate the time evolution of the monomer conversion and the degree of polymerization over the whole course of the reaction. Parouti *et al.*, (2003) reported a comprehensive experimental investigation on the batch and semibatch emulsion terpolymerisation of methyl methacrylate/butylacrylate/ acrylic acid (MMA /BuA /AA). The role of the non-ionic surfactant octylphenoxypolyethoxyethanol in emulsion polymerization of styrene, butyl acrylate as well as their copolymerization were investigated previously (Ozdeger *et al.*, 1997a; 1997b; 1997c) using the calorimetry as the main tool for the kinetics analysis. Chern, (2006) reported that batch emulsion polymerization is commonly used in the laboratory to study reaction mechanism, develop new latex products and obtain kinetic data for process development and reactor scale-up. In recent times, there has been growing interest in the use of special liquids called ionic liquids (ILs) as solvents for chemical reactions. ILs are salts that are liquid at room temperature. The interest in the use of ILs is stimulated not only by their green nature and cleaner chemical process but also by novel set of polymers that may be generated by their inclusion as reaction media. Although, the research on using ILs in polymer synthesis is still in its infancy. the few reports on the use of ionic liquids in classical free radical polymerization revealed that even higher molecular weight polymers were obtained in comparison with organic solvents (Hong *et al.*, 2002; Chen *et al.*, 2004 and Wu *et al.*, 2005). A wide variety of organic transformations have been demonstrated in ILs, often with increased conversion, faster rates of reaction, and greater

ease of product isolation (Welton, 1999 and Zhao *et al.*, 2002). In the report of Kubisa (2003), ionic liquid are composed of bulky 1,3-dialkylimidazolium, alkylammonium, alkylphosphonium or alkylpyridinium organic cations and inorganic anions such as most frequently AlCl_4^- , BF_4^- or PF_6^- but also NO_3^- , ClO_4^- , CF_3COO^- , CF_3SO_3^- , or CH_3COO^- . It is therefore clear that it is possible to form any specific IL composition depending on the user's need and that the desired physical, chemical and biological properties can be realized in a single salt by proper selection of the component ions or in the mixtures of component ions. In the report of Carlin *et al.*, (1990), Chloroaluminate-based ILs have been investigated as solvents for ethylene polymerization. The polymerization of methylmethacrylate (MMA) in ILs were investigated by Schmidt-Naake *et al.*, (2008), Strehmel *et al.*, (2004), Vygodskii *et al.*, (2005) and Honge *et al.*, (2002). The latter studied the free radical polymerization of MMA in several ILs and found that the polymer formed in ILs have molecular weight up to ten times higher than samples synthesized in benzene. Benton and Brazel (2002, 2004) used 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM]PF₆) and found that the degree of polymerization was five times in ([BMIM]PF₆) than in benzene. However, Shamsuru and Abdullah (2010) and Ghandi (2014) reported the strong limitations of ILs such as their reaction with some reactants making it unfit to be considered as inert solvents and their impracticability for industrial scale application as a result of their non-availability and high cost.

Biodiesel has been considered as a bio-solvent in the solution polymerization of styrene in this study. This aspect is actually of great interest not only because the process is environmentally benign, but also the possibility for the preparation of a variety of new functional materials coupled with the apparently limited number of published works on the solvency power of biodiesel. Furthermore, the unavailability of reports on styrene polymerization using biodiesel

from pawpaw seeds and waste cooking oil provides an attraction to investigate the potential for solvency from biodiesel such as pawpaw and waste cooking oil source. Biodiesel is made entirely from vegetable oil or animal fats, it is renewable, environmentally benign (bio-degradable) and does not contain any sulphur, aromatic hydrocarbons, metals or crude oil residues (Dube *et al.*, 2007). Mcmanus *et al.*, (2004) in their report stated that biodiesel has high boiling point. This means it will not pose a hazard in the workplace due to evaporation and reactions can be carried out at elevated temperature without fear of excessive pressure build up. Sherman *et al.*, (1998) reported that many of solvents are known to upset our ecosystem by depleting the ozone layer and participating in the reactions that form topospheric smog or pose hazardous threats to the environment. In addition, some solvent may cause cancer, some are neuro-toxins, or may cause sterility in those individuals frequently exposed to them (Table 6), some solvents have been regarded as GRASS (generally regarded as safe solvents) while some are not in terms of usage (Table 7). Ideally, solventless reaction should be developed but unfortunately, synthetic reactions are solvent based and are likely to be so till eternity. They are needed industrially for the solvation of reactants though care has to be taken in terms of their selection. When such inevitable need arises, the solvent should be non-toxic, non-flammable and eco-compatible. There is therefore a clear need to search for alternative solvents to minimize the problems inherent in solvent release to the environment which is part of our focus in this study. Recently, non-classical solvents such as supercritical fluids have been considered as an alternative reaction media (Duan *et al.*, 2006). Supercritical CO₂ has been used in the manufacture of fluoropolymers as a replacement solvent for 1, 1, 2 – trichloro - 1, 2, 2-trifluoroethane, the implementation however created corrosion problems (Romack *et al.*, 1995). Considering economic reason, one can surmise that supercritical fluids may not be a convenient

solvent alternative. Biodiesel obtained from pawpaw seed oil (PSO) and waste cooking oil (WCO) have been selected as bio-solvents for the styrene polymerization in this study. PSO is inedible oil. Apart from the potential impacts on food security, values are also gradually been created for the pawpaw seeds instead of been disposed which most of the time is done indiscriminately. There is also a well structured supply line for WCO in developed countries. An instance of that of the United States of America is shown in Table 8.

2.8. Batch Reactor System for Styrene Polymerization

Despite the large tonnage involved in the industrial production of this commodity polymer, autoclave (batch) reactors are still used almost exclusively and it has been adopted in this study at the laboratory level. However, Mohammadi *et al.*, (2014) in his studies considered spinning disc reactor (SDR) as an ideal reactor for conducting batch free radical polymerization. The control of polymerization reactor conditions is key for desirable polymer properties at reduced cost and time (Vasco de Toledo *et al.*, 2005). Kee and Kyu (1988) reported that in many industrial polymerization processes, a variety of initiator systems are practiced to produce polymers of various grades to meet diversified end use requirements and made a special recommendation for multifunctional initiators.

Table 8: Selected restaurants in the City of Gainesville (U.S.A) to determine supply lines for waste cooking oil.

Restaurant	Years in Business	Volume of waste oil disposed per month in gallons	Amount paid for disposal per month in dollars
Miraku	1	117 lbs	Free
Sandy' place	1 and 2 months	80	Free
Las Magarita	5	100	120
Moraghot	2.5	160 lbs	Free
Boston Market	8	100	150
JP Gators	20	50 lbs	Free
Napolatona	12	300 lbs	<10
Calypso Bar and Grill	1.5	72-80	Free
El Toro	14	600 lbs	40
Mildred's Café	8.5	30	Free
Chik-Fil-A	24	1052 lbs	Free
Kotobuki	14	600 lbs	Free
Ballyhoo Bar and Grill	3	3400 lbs	511-550 per year
Porter's	4	20	80
Clara's	1	420	150
Hot Wok	10 months	100	230
Mr.Han's Restaurant and Bar Club	17	140	60
Miya Sushi	8	12	100
Timber Creek Steakhouse	12	560	130

Owolabi *et al.*, (2011)

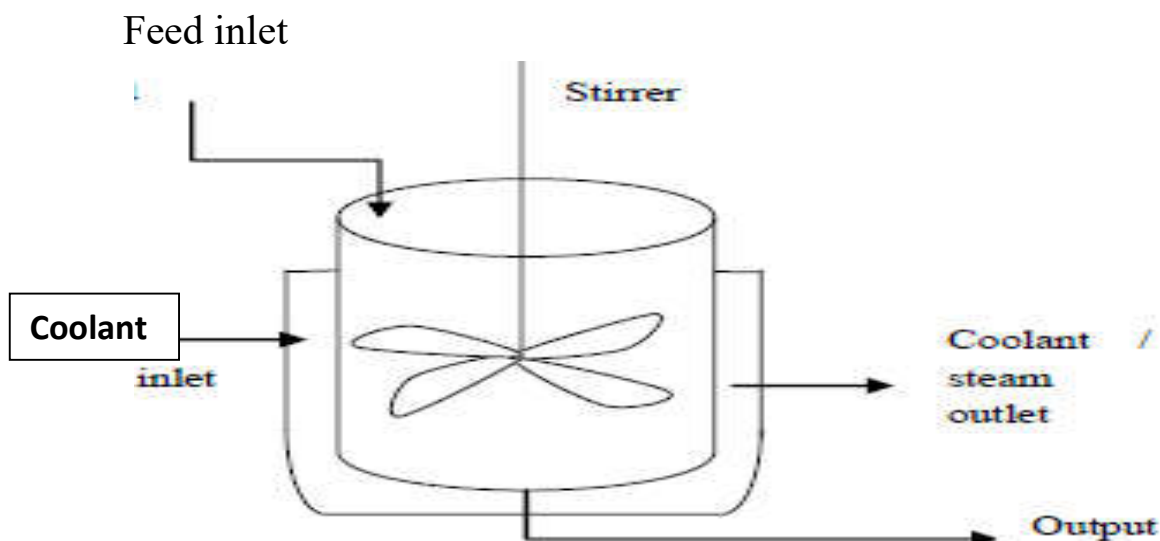


Figure 5: Schematic diagram of batch polymerization reactor

2.9. Styrene Polymerization Optimization

There is a growing awareness about the production and use of PS. Consequently, the grade of polymer is expected to face increasing pressure for cost reduction and production of polymer that will continue to stand the test of time (Figures 1-2). Efforts to improve the productivity of these processes are directly related to the reduction of the time required to complete each batch, for a given polymer quality (average molecular weight, polydispersity, etc.). This can be achieved by the use of various initiators introduced only at the beginning of the polymerization process, thereby avoiding the use of a continuous dosage system and its associated control challenge. The initiator mixture, adequately formulated for a given polymer grade, according to the existing reactor capacity and heat removal system. Kee and Kyu (1988) reported that in many industrial polymerization processes, a variety of initiator systems are practiced to produce polymers of various grades to meet diversified end use requirements and made a special recommendation for multifunctional initiators. The role of reduction in reaction time played by multi-functional initiators is in the report of Almeida *et al.*, (2008). Wu *et al.*, (1982) in his work connected the

structure-property relations of polymer to the molecular weight distribution and its mean value such as weight and number average degree of polymerization. Kee and Kyu (1988) in addition established that with properly chosen multifunctional initiators, it is possible to achieve both high monomer conversion and significantly high molecular weight polymers simultaneously. The process optimization objective here is to obtain the best possible styrene monomer conversion within the shortest possible time with PS of desired end use quality in a consistently safe manner. The classical method of optimization reported about three decades ago by Akhnazarova and Kafarov (1982) and Box *et al.*, (1978) involved process variable optimization by changing one variable at a time and keeping the others at fixed levels. This method is not only time consuming but also does not guarantee the determination of optimal conditions. The method also does not consider the interactive effects among process variables thus limiting inferences drawable from the parametric studies of various processes. It is also called the traditional one-variable-at-a-time optimization technique which was formerly common among researchers of optimization studies (Marcos, 2008). This means while one process variable is changed, others are kept constant. The method further increases experimental time, energy and budget. Many other researchers as discussed have optimized processes using other different approaches. Kittima and Nanthiya (2013) and others such as Arayaprane and Rempel (2004), and Helmiyati *et al.*, (2010) reported that reaction conditions are generally developed to probe the relationships between monomer conversion and polymerization conditions. To achieve high performance and cost effective PS with inherent properties, the optimization of the process is a key factor to be considered. Ray (1967) used a gradient technique to illustrate the optimization of polymerization in series of continuous stirred tank reactors (CSTRs). Osakada and Fan (1970) used several weighted end condition and time integral objective functions to determine control policies for temperature and

catalyst feed rate in the CSTRs. Kiparissides *et al.*, (2002) under the significant model parameter uncertainty approach carried out an on-line optimizing control of the number and weight average molecular weights and the weight chain length distribution of the polymer product in a free radical batch polymerization reactor. Ramezani (2010) also reported the Taguchi method of experimental design using the Win Robust Software (Version 1.0) to determine the optimum conditions for castor oil trans-esterification reaction. Many other authors such as Arayaprane *et al.*, (2003, 2006); Arayaprane and Rempel (2004); Dhib and Hyson (2002); Delfa *et al.*, 2009); and Hanai *et al.*, (2003) made use of less complicated tools such as RSM and ANN to investigate the inter-relationship without a prior knowledge of the reaction mechanism. RSM is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables (Montgomery, 2009). It enables simultaneous varying of process variables, unlike what is obtainable in conventional experimentation, thereby eliciting the interaction between such variables. It also provides a model equation relating the response parameter to the process variables and optimization of same. It is a veritable tool that has been deployed in a wide range of fields namely; transesterification (Betiku *et al.*, 2015; Muppaneni *et al.*, 2013), solvent extraction (Rai *et al.*, 2016; Mohammadi *et al.*, 2016), adsorption (Ahmed and Theydan, 2014; Ezechi *et al.*, 2015), Fenton process (Kumar and Pal, 2012), drying operations (Krishnaiah *et al.*, 2015), carrageenan production (Bono *et al.*, 2014) etc. Similarly, other reports such as those of Somnuk *et al.*, (2013), Jain *et al.*, (2011), Patil *et al.*, (2011), Pereda-Ayo *et al.*, (2011), Gopinath *et al.*, (2010), Contesini *et al.*, (2009) among others confirmed the wide use of the RSM to develop, improve and optimize various processes. In polymer and related field, RSM has found application in some reported studies (Ghasemi *et al.*, 2010; Lee *et al.*, 2011; Nasef *et al.*, 2011; Banerjee *et al.*, 2012;

Chieng *et al.*, 2012; Zheng *et al.*, 2015; Rojo *et al.*, 2015; Razak *et al.*, 2015; Fattahpour *et al.*, 2015; Hirzin *et al.*, 2015; Davoudpour *et al.*, 2015). Razali *et al.*, (2015) used RSM to study the grafting of polydiallyldimethylammonium chloride (PolyDADMAC) to cassava starch using potassium persulfate (KPS) as a free radical initiator. Four variables were investigated via central composite design (CCD) namely; mole ratio of Diallyldimethylammonium Chloride (DADMAC) to starch, reaction time, reaction temperature and initiator concentration to determine their individual and interactive effects on the grafting percentage. They obtained satisfactory results as the actual experimental yield at optimized conditions was very close to the value predicted by their derived model. Aroonsingkarat and Hansupalak (2013) studied the effect of processing conditions on monomer conversion in the graft copolymerization of polystyrene and rubber using RSM via CCD. The reaction temperature, time, percentage of deproteinized rubber, and amount of chain transfer agent were the four variables investigated. In a related study, Sresungsuwan and Hansupalak (2013) investigated the influence of processing conditions on the mechanical properties of compatibilized styrene/natural rubber blend using CCD. No such study has been reported in the literature for solution polymerization of styrene. The study of Zheng *et al.*, (2014) focused on condensation polymerization process, however no known report to the best of our knowledge has been presented on addition polymerization process, the case of which is being considered in this research. Usually, the use of RSM determines a polynomial function that expresses how a dependent variable is affected by process variables. The magnitude of the coefficients in the polynomial function is an indication of the significant level of effects of single and interactive process variables on the response (Mao *et al.*, 2007, Rodriguez-Nogales *et al.*, 2007). The optimization of process variables principle in RSM is to obtain the maximum or minimum response (Xiao and Zhu, 2010, Bezerra *et al.*, 2008). Apart from the central composite

design (CCD) which was adopted in this study, the Box-Behnken is another example of RSMs that have been used in optimization studies, interactions and influence of polymerization conditions on polymer yield (Nasef *et al.*, 2011, Banerjee *et al.*, 2012). The second phase of the research herein is the development of statistical models that correlate process conditions to styrene monomer conversion using the CCD approach and the subsequent determination of optimal operating strategy. Such models and strategy save time, energy and funds by reducing the number of additional experiment. However, ANNs are considered a better approach to RSMs in situation where a complex function rather than where mere polynomial relationship exists between the process variables and the response. The main objective herein is to develop a robust model that is user friendly and hence may be suitable enough for industrial applications.

CHAPTER THREE

3.0

METHODOLOGY

This chapter presents the details of materials, reagents and apparatus including the experimental set-up and procedures for styrene polymerization in solvent media. The detailed reaction mechanism and kinetic models development and validation for parameter estimation were also presented. The optimization procedure adopted and the analysis of the PS samples were also described.

3.1. Materials and Reagents Used

3.1.1 Apparatus

The under listed (section 3.1.1 and 3.1.2) were the reagents and apparatus used during the experimental stage.

Heater (Model SH-2 41121800) with a magnetic stirrer equipped with temperature controller; ace round-bottom pressure flask with thermo-well; transparent plastic petrish dish; pyrex beaker; glass separating funnel; soxhlet extractor (model Z564788) with capacity 145 ml, glass rod; Ubbelohde viscometer (model UBBEL01NC) equipped with a capillary tube; measuring cylinder, stop watch, shaking water bath (model Z741416) equipped with digital temperature controller, thermometer (0 - 200 °C).

All the glassware prior to polymerization were inspected to ascertain that there was no trace of dirt or remnants of materials. Glass reactor was preferred to stainless steel in this study to view and monitor the reaction as it progresses and to further prevent radical reaction interference with the alloy wall (Fe, Cr, Ni, C) of the stainless steel reacting vessel. A 100 ml Ace round-bottom pressure flask with thermo-well that can withstand a maximum pressure of 60 psig at 120 °C was used as the reactor. Other reactions at lower temperatures were carried out in sealed 100 ml

pyrex beakers placed in water bath equipped with vibratory/perturbatory facility and digital temperature controller.

3.1.2 Reagents

Styrene (99 %) inhibited with 10–15 ppm 4-tertbutylcatechol; benzoyl peroxide (75 %); Benzoyl peroxide blend with dicyclohexylphthalate (contains 0.5 % water); Methanol (CH_3OH) (99.8 %); Sodium sulphate (Na_2SO_4) (99 %); Sodium hydroxide (NaOH) (98 %); 2, 2 - Azobis (2-methylpropionamidine) dihydrochloride (AIBA); Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$); sodium dodecyle sulphate (SDS) $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}$; Acetone (99.9 %) (CH_3)₂CO; Chloroform (CHCl_3) (99%); Benzene (99 %) C_6H_6 ; Toluene (99.8 %) $\text{C}_6\text{H}_5\text{CH}_3$; Ethylacetate ($\text{CH}_3\text{COOCH}_2\text{CH}_3$); Acetonitrile CH_3CN ; dimethylsulphoxide (CH_3)₂SO; Distilled and De-ionised water. All the reagents used were of analytical grade, purchased from Sigma Aldrich in Germany and used as received except for styrene monomer which was de-stabilized.

3.2. De-Stabilization of the Styrene Monomer

To prevent the styrene monomer from self reacting while in storage, stabilizers or inhibitor are added by the manufacturer. The inhibitor needed to be removed prior to its use for polymerization. The removal was done using the procedure reported by Arai and Saito (1976) and Arai *et al.*, (1986). The styrene monomer (100 ml) which contains phenol (often 4-tert-butylcatechol) as a polymerization inhibitor was added to 100 ml of 10 % NaOH solution. The mixture was strongly shaken and was allowed to settle by gravity in a separating funnel. The bottom layer consisting of the inhibitor was carefully drained.

3.3. Extraction of Oil from (Pawpaw) *Carica papaya* Seeds

Average sized and matured pawpaw fruits about fifty in number were purchased from Ketu Market (a local market) in Lagos metropolis of Nigeria (Latitude 6.5833 and Longitude 3.75). They were prepared for use by cutting into two longitudinal halves. The seeds were removed manually, sun dried for several days and then kept in a sealed bottle under cool dry storage. More seeds were obtained directly from pawpaw fruits sellers at Moremi (Female Students) Hall and at the second gate of the University of Lagos. The sun dried seeds were ground into fine powder with a Marlex blender (with trademark 277985) manufactured by Kanchan International Limited, Dabhel in India. A Soxhlet extractor was used for solvent extraction of the oil. The solvent (n-hexane) was removed from the extract by distillation and the residual oil component was collected and used for the experimental work. A 500 ml capacity soxhlet extractor was used in the extraction of the oil from the ground seeds. Four packs of 5 g of the ground pawpaw seeds (a batch) were packed in a Whatman filter paper and inserted into the soxhlet extractor while 350 ml of n-hexane was used as the extracting solvent. The period of continuous extraction was 2 hours. By this time, the batch of packed seeds had been de-oiled as evidenced by the continuous clear appearance of the condensed vapour from the solvent. The four packs of 5 g of the ground pawpaw seeds were oven dried at 65 ± 2 °C for 30 minutes until a constant weight was observed. The solvent was recovered by simple distillation and the residual oil was also oven-dried at 40 ± 2 °C for about 20 minutes as suggested by Ofoegbu *et al.*, (2006). The oil was then transferred to an air tight glass container and allowed to cool, before being weighed. (The drying, cooling and weighing was repeated until a constant dry weight was obtained, to within 0.01 g.)

3.4. Purification of Waste Cooking Oil

Vegetable oil after being used to fry large size fish several times for a considerable number of days in an extended household in Lagos metropolis of Nigeria (Latitude 6.5833 and Longitude 3.75) was collected in a 2 litre bottle. The oil was de-odourised and purified as thus; accurately prepared 0.73 % NaCl solution was poured in the spent oil contained in a separating funnel and shaken rigorously for about 15 minutes. After it was allowed to settle by gravity, the bottom sediments were removed. A mixture of chloroform, methanol and 0.58 % of NaCl solution in the ratio 5:48:47 (Mohammed, 2011) was added to the partially purified oil in the separating funnel to completely de-odourise the oil. Shaking took place for another 15 minutes followed by gravitational settling and later removal of the second sediments. The purified oil was poured in a beaker of wider surface area and placed in a water bath to enable any residual solvent to escape.

3.4.1 Gas Chromatography Mass Spectrometry (GC-MS) analysis of Oil

The composition of WCO was analyzed by GC-MS on a 6890 Gas Chromatograph equipped with a 5973N Plus Mass Spectrometer. Oxygen-free nitrogen was used as carrier gas at a flow rate of 1.0 ml/min.

3.5. Trans-Esterification of the Oil with Methanol

Biodiesel from Pawpaw Seed Oil and Waste Cooking Oil were obtained by a simple trans-esterification reaction between methanol and the respective oils in the ratio 6:1 at reaction conditions; 60 °C temperature, 0.75 wt % amount of NaOH catalyst and reaction time of 60 minutes under agitation for maximum yield (Kang and Wang, 2013). The biodiesel obtained

from the pawpaw seed oil surprisingly solidified with time indicating the presence of phospholipids in the oil (gum). The oil was later de-gummed using 2.5 ml of 85 % H_3PO_4 diluted with 30 ml of water. The mixture with the oil was placed in a water-bath for 5 minutes at 60 °C before agitating the mixture in a shaker at 300 rpm for 30 minutes. The resulting mixtures were placed in a centrifuge at high speed for phase separation.

3.6. Polymerization of Styrene

The styrene polymerization was conducted in a 62 mm diameter round bottom pressure flask with thermo-well. The reaction initiators include benzoyl peroxide, benzoyl peroxide blend with dicyclohexylphthalate), 2, 2 – Azobis (2- ethylpropionamidine) dihydrochloride (AIBA) and potassium persulfate. The solvents of different polarities used for the study include acetone, chloroform, benzene, toluene, acetone / chloroform mixture, ethyl acetate, acetonitrile, dimethylsulfoxide (DMSO), distilled and de-ionised water (DDW); and biodiesel obtained from pawpaw seed oil and waste cooking oil. In each study run, specific amount of BPO and styrene monomer concentration (8.612 M) were dissolved in specific volume of solvent to maintain a monomer to solvent ratio of 1:1, 1:2, 1:3, and 1:4 (typically, 5 ml of styrene to 5 ml of solvent represents 1:1). The reaction temperature maintained at 120 °C (± 2 °C) under agitation provided by a magnetic driven bar stirrer at a speed of about 500 rpm. For reactions at lower temperature (60 °C and 90 °C), polymerization reactions were performed in sealed 100 ml glass beakers (71 mm length, 51 mm diameter) in a water bath equipped with a shaker and a digital temperature controller. At 10 minutes interval of reaction time, the reactor was opened up and cooled to collect the resulting polymer solution. The clear polymer solution was added to about 3 ml of methanol in a beaker with continuous stirring to precipitate the polymer. The upper clear solvent was decanted while the bottom polymer samples were air-dried to remove excess solvent and

dried for 2 weeks at room conditions until a constant weight was reached. Monomer conversion was determined by gravimetric method. All samples were identified with a digit, two letters and two other digits. The first digit corresponds to the volume ratio of solvent used, the two letters styrene and the respective solvent used. The first digit of other two corresponds to the volume ratio of the styrene monomer and the last corresponds to order of appearance of the styrene–solvent combination. For instance, sample 1SA12, stands for 1 volume ratio of acetone in styrene acetone combination for such second combination.

3.7. Polymer Precipitation and Solvent Removal / Recovery

The clear polymer solution was added to about 3 ml of Methanol in a beaker with continuous stirring to precipitate the polymer (Somaieh and Marc, 2008). The top clear solvent was decanted while the bottom polymer samples were air-dried to remove excess solvent and dried for 2 weeks at room conditions until a constant weight was reached.

3.8. Post Polymerization Analysis

Monomer conversion into polymer and polymerization rate were estimated using Eqs.(1-4). The synthesized polymers were further subjected to solubility and density tests in various solvents and their molecular weights were also determined. The styrene conversion was determined gravimetrically while the PS molecular weights were determined using solution viscosity molecular weight method. The IR spectra of polymers dispersed in KBr discs using Perkin Erlmer spectroscopy was carried out. The PS samples were pulverized for further analysis.

3.9 Characterization of PS

The sample prepared with optimum processing conditions only (optimized sample) was characterized. The IR Spectra of the sample dispersed in KBr discs was done using Perkin Erlmer Spectroscopy. The melting point determination, and chemical resistance evaluation using ethanol, water and tetrahydrofuran were carried out.

3.10. Parameter Estimation, Reaction Mechanism, Kinetic model development, model validation and Optimization

3.11. Parameter Estimation

3.11.1 Monomer Conversion and Estimation of Polymerization Rate

The monomer conversion into polymer (% conversion) as well as rate of polymerization (Rp) were gravimetrically determined (Dry weight method).

$$\% \text{ conversion} = \frac{\text{mass of polymer}}{\text{mass of monomer}} \times 100 \quad (1)$$

This is in form of the mass concentration, it could also be in the form of molar concentration

$$\begin{aligned} \% \text{ Conversion} &= \frac{[\text{Polymer}]}{[\text{Monomer}]} \times 100 \\ \% \text{ Conversion} &= \frac{\text{volume of polymer}}{\text{volume of monomer}} \times 100 \end{aligned} \quad (2)$$

The polymerization rate (Rp) is gravimetrically calculated as :

$$R_p = \frac{[\text{Polymer}]}{\text{Reaction time}} \left\{ \frac{\text{Mol}}{\text{l.s}} \right\} \quad (3)$$

$$\text{Where } [\text{Monomer}]_0 = \left[\left(\frac{\% \times \text{density of monomer}}{\text{Molecular Weight of monomer}} \right) \times 10 \right] \text{ (Sigma Aldrich, 2013)} \quad (4)$$

3.11.2 Polymer Molecular Weight Determination

The molecular weight of the polymer sample was determined using solution viscosity method described in Bello (2001). Viscosities of polymer solutions were measured with toluene as solvent at 30 °C using Ubbelohde glass viscometer. In viscosity method, the time taken for the polymer solution to flow through the capillary is compared with the time for a pure solvent. If the flow time for the solvent is t_0 and that of polymer solution is t , the relative viscosity is defined as:

$$\eta_r = \frac{t}{t_0} \quad (5)$$

The specific viscosity, $\eta_{sp} = \eta_r - 1 = \frac{t-t_0}{t_0}$ (6)

The Solomon Gatesman and Ciuta (Eq.7a), Kuwahara (Eq.7b) and Rao and Yaseen (Eq.7c) equations were used to determine the intrinsic viscosity:

$$\eta = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{c} \quad \text{Baastiaan (2005)} \quad (7a)$$

$$\eta = \frac{\eta_{sp} + 3 \ln \eta_r}{4c} \quad \text{Charlier *et al.*, (2015)} \quad (7b)$$

$$\eta = \frac{\eta_{sp} + \ln \eta_r}{2c} \quad \text{Charlier *et al.*, (2015)} \quad (7c)$$

where C is the concentration (g/ml) of the sample. It is important to note that the intrinsic viscosity is not the viscosity as such but the volume per unit mass that the polymer occupies in a solution.

The Mark-Houwink-Sakurada (MHS) Equation for viscosity of polyethylene and polystyrene (Wagner, 1985) was used to calculate the intrinsic viscosity molecular weight.

$$\eta = KM^a \quad (\text{Bello, 2001 and Wagner, 1985}) \quad (8)$$

K and a are constants which are dependent on the solvent, the type of the polymer and the temperature (Table 9).

Table 9: Recommended value of Mark-Houwink constants for polystyrene.

Solvent	Temp. °C	K(ml/g) x 10⁻⁴	a	Molecular weight Range x 10⁻⁵
Toluene	-----	1.28	0.70	5.5-20.5
Toluene	-----	0.55	0.80	1.1-3.4
Toluene	-----	0.01	1.12	1.1-1.7
Toluene	30	3.7	0.62	2.0-18
Butanone	40	7.0	0.53	2.0-18

(Goldberg, 2003)

Table 10 shows the rate expressions of each of the elementary steps (both the main and side reactions) at different stage of the styrene polymerization.

Table 10: Kinetic mechanism of styrene polymerization adopted

S/N	Polymerization Stage	Polymerization Mechanism	Reaction Rates (This Study)
Main Reactions			
1.	Initiator Decomposition	$I \xrightarrow{k_d} 2R^\bullet$	$r_I = k_d C_I$ $r_{R^\bullet} = 2fk_d C_I$
2.	Chain Initiation	$R^\bullet + M \xrightarrow{k_I} P_1$	$r_{R^\bullet} = k_I C_M C_{R^\bullet}$ $r_M = k_I C_M C_{R^\bullet}$ $r_{P_1} = k_I C_M C_{R^\bullet}$
3.	Propagation	$P_i + M \xrightarrow{k_p} P_{i+1}$	$r_{P_i} = k_p C_{P_i} C_M$ $r_{P_i} = k_p C_{P_{i-1}} C_M$ $r_M = k_p C_M \sum_{i=1}^{\infty} C_{P_i}$
4.	Termination by Combination	$P_i + P_j \xrightarrow{k_{tc}} D_{i+j}$	$r_{P_i} = k_{tc} C_{P_i} \sum_{j=1}^{\infty} C_{P_j}$ $r_{P_j} = k_{tc} C_{P_j} \sum_{i=1}^{\infty} C_{P_i}$ $r_{D_i} = \frac{1}{2} k_{tc} C_{P_{i-j}} \sum_{j=1}^{i-1} C_{P_j}$
Side Reactions			
5.	Chain Transfer to Monomer	$P_i + M \xrightarrow{k_{trm}} P_i + D_i$	$r_{P_i} = k_{trm} C_{P_i} C_M$ $r_M = k_{trm} C_M \sum_{i=1}^{\infty} C_{P_i}$ $r_{D_i} = k_{trm} C_{P_i} C_M$ $r_{P_1} = k_{trm} C_{P_i} C_M$
6.	Chain Transfer to Polymer	$P_i + D_j \xrightarrow{k_{trp}} D_i + P_j$	$r_{P_i} = k_{trp} C_{P_i} \sum_{j=1}^{\infty} j C_{D_j}$ $r_{P_i} = k_{trp} i C_{D_i} \sum_{j=1}^{\infty} C_{P_j}$ $r_{D_i} = k_{trp} i C_{D_i} \sum_{j=1}^{\infty} C_{P_j}$ $r_{D_i} = k_{trp} C_{P_i} \sum_{j=1}^{\infty} j C_{D_j}$ $r_{LCB} = k_{trp} \sum_{i=1}^{\infty} C_{P_i} \sum_{j=1}^{\infty} j C_{D_j}$
7.	Chain Transfer to Solvent	$P_i + S \xrightarrow{k_{trs}} D_i + P_i$	$r_{P_i} = k_{trs} C_{P_i} C_S$ $r_{D_i} = k_{trs} C_S \sum_{i=1}^{\infty} C_{P_i}$ $r_S = k_{trs} C_S \sum_{i=1}^{\infty} C_{P_i}$

where I = initiator, R^* = generated radical, M = monomer, P_i = growing polymer of length i , D_j = dead polymer of length j , S = solvent.

Kiparissides *et al.*, (2006), Pladis and Kiparissides (1998), Achilias and Kiparissides (1992), Garg *et al.*, (2014), Kiparissides *et al.*, (2006), and many others reported the inclusion of the f term in the reaction rate corresponding to serial number 1 in Table 10. When the radicals are formed upon initiator decomposition; they need to reach monomer molecules to form the primary radicals. However, due to several mechanisms induced by impurities and chemical species like solvent present in the reaction mixture, many radicals are destroyed or consumed before reacting with monomer. Thus, only a fraction (f) of radicals formed are able to form these primary radicals. Similarly,

Kiparissides *et al.*, (1993) in their report observed that one of the most important problems in simulating the operation of industrial high pressure polymer reactors is the selection of appropriate values of the various rate constants. Examination of literature values of rate parameters often reveals a very wide range of reported values in spite of the great number of papers published on the modeling of polymer reactors. Gupta *et al.*, (1985), Ehrlich and Mortimer (1970), Goto *et al.*, (1981), Lee and Marano (1979), Takahashi and Ehrlich (1982), Thies and Schoenemann (1970), Brandolin *et al.*, (1996), Dhib and Al-Nidawy (2002), and Kiparissides *et al.*, (1993) in their reviews attributed the inconsistency of published set of rate constants to the complexity of the reaction, the large number of kinetic parameters to be determined experimentally and the wide range of experimental conditions over which the kinetic parameters were estimated. For comparison of research outcomes and also to overcome the wide divergence in literature values of kinetic parameters for free radical polymerizations under ostensibly the same conditions, agreed values are given to some fundamental kinetic parameters

for simple monomers [Brandolin *et al.*, (1996), Dhib and Al-Nidawy (2002), and Kiparissides *et al.*, (1993)]. The work of Hui and Hamielec (1972) remained a point of reference in terms of rate constant values. However, for consistency, the rate constant values as adopted by Garg *et al.*, (2014) have been used in this study (Table 11).

Table 11: Rate constant of elementary steps

S/N	Kinetic Model Parameters	Reference
1.	k_p (Lmol ⁻¹ min ⁻¹) = $6.54 \times 10^8 \exp(-7051/RT)$	Garg <i>et al.</i> , (2014)
2.	k_{fm} (Lmol ⁻¹ min ⁻¹) = $1.38 \times 10^8 \exp(-12670/RT)$	
3.	k_t (Lmol ⁻¹ min ⁻¹) = $7.53 \times 10^{14} \exp(-1677/RT)$	
4.	k_d (min ⁻¹) = $1.69 \times 10^{14} \exp(-25383/RT)$	
5.	k_{fs} (Lmol ⁻¹ min ⁻¹) = $9.95 \times 10^{10} \exp(-11,000/T)$	
6.	k_{ic} (Lmol ⁻¹ min ⁻¹) = $2.67 \times 10^8 \exp(-2.084/RT)$	
7.	f = 0.5	Fogler (1999)
8.	M_0 (Styrene) = 8.612 mol/L	This study
9.	Molecular Weight of Styrene (M_w) = 104.15	
10.	Temperature = 393, 363 and 333K	
11.	S_0 (Acetone) = 13.38 mol/L	
12.	I_0 (Initiator) = 0.0825 mol/L , 0.0620 mol/L , 0.0413 mol/L, 0.0206 mol/L	
13.	R = 1.987 cal/mol.K	

where k_d = Initiator dissociation rate constant

k_{fm} = Chain transfer to monomer

k_t = Termination rate constant

k_p = Propagation rate constant

k_{fs} = Chain transfer to solvent

M_0 = Initial monomer concentration

R = Universal gas constant

S_0 = Initial solvent concentration

I_0 = Initial initiator concentration

3.12. Kinetics Model Development

For easy expression of the kinetic rate equation using the above kinetic scheme (Table 10), the following assumptions on modeling of free radical polymerization were made;

3.12.1. Modeling and Computational Assumptions

- i. Steady state approximation for radicals.
- ii. The reaction rate constants are independent of chain lengths.
- iii. All the reactions are irreversible and elementary
- iv. The reactor contents are perfectly mixed
- v. Radicals generated are of equal reactivity (Flory's principle) Constant reactor pressure.
- vi. Constant initiator efficiency.
- vii. Rate constants are independent of viscosity

3.12.2 Mass and Molar Balances for all Species Present (Monomer, Initiator, Solvent, Live Radical and Dead Polymer)

Rate equation was established for each of the reaction steps (Table 10). The Garg approach was employed in this aspect of the research. The mass balance of the chemical species in an ideal batch reactor was carried out and transformed into equations in terms of moment. The method of moments is based on the statistical representation of the molecular properties of interest e.g weight - average molecular weight (M_w), number-average molecular weight (M_n) in terms of the leading moments of the respective distributions, (Arriola, 1989). Accordingly, the leading moments of the total number chain length distributions (TNCLDs) of live and dead polymer chains are defined as:

$$\text{Live:} \quad \lambda_k = \sum_{i=1}^{\infty} i^k [P_i] \quad (9)$$

$$\text{Dead:} \quad \mu_k = \sum_{j=1}^{\infty} j^k [D_j] \quad (10)$$

The Number average molecular weight (M_n) and the weight average molecular weights (M_w) can be expressed as

$$M_n = M_w \frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0} \quad (11a)$$

$$M_w = M_w \frac{\lambda_2 + \mu_2}{\lambda_1 + \mu_1} \quad (11b)$$

$$\text{Polydispersity index (PDI)} = \frac{M_w}{M_n} = \frac{(\lambda_2 + \mu_2)(\lambda_0 + \mu_0)}{(\lambda_1 + \mu_1)^2} \quad (11c)$$

There is need to generate six equations (Eqs.12-17) from the chemical mass balances to calculate the six moments ($\lambda_0, \lambda_1, \lambda_2$ and μ_0, μ_1, μ_2) for the determination of molecular weight distribution

$$\frac{1}{V_R} \frac{d(\lambda_0 V_R)}{dt} = 2fk_d I - (k_{tc} + k_{td})\lambda_0^2 = 2fk_d I - k_t \lambda_0^2 \quad (12)$$

$$\frac{1}{V_R} \frac{d(\lambda_1 V_R)}{dt} = 2fk_d I + (1 + R_{SM})k_{pr}M\lambda_0 - k_t \lambda_0 \lambda_1 - (R_{MM} + R_{SM})k_{pr}M\lambda_1 \quad (13)$$

$$\frac{1}{V_R} \frac{d(\lambda_2 V_R)}{dt} = 2fk_d I + (1 + R_{SM})k_{pr}M\lambda_0 + 2k_{pr}M\lambda_1 - k_t \lambda_0 \lambda_1 - (R_{MM} + R_{SM})k_{pr}M\lambda_2 \quad (14)$$

$$\frac{1}{V_R} \frac{d(\mu_0 V_R)}{dt} = (R_M M + R_S S) k_{pr} \lambda_0 + (1 - \frac{R_T}{2})k_t \lambda_0^2 \quad (15)$$

$$\frac{1}{V_R} \frac{d(\mu_1 V_R)}{dt} = (R_M M + R_S S) k_{pr} \lambda_1 + k_t \lambda_0 \lambda_1 \quad (16)$$

$$\frac{1}{V_R} \frac{d(\mu_2 V_R)}{dt} = (R_M M + R_S S) k_{pr} \lambda_2 + k_t \lambda_0 \lambda_2 + R_T k_t \lambda_1^2 \quad (17)$$

$$\text{where } V_R = \text{Volume of solution at any time } t, L \quad (17a)$$

$$I(\text{Initiator concentration, mol/L}) = I_0 e^{-k_d t} \quad (17b)$$

$$M(\text{Monomer concentration, mol/L}) = M_0 \exp[-B_0(1 - e^{-k_d t})] \quad (17c)$$

$$S(\text{Solvent concentration, mol/L}) = S_0 \exp[-R_S B_0(1 - e^{-k_d t})] \quad (17d)$$

$$B_0 = \sqrt{\frac{8fk_{pr}^2 I_0}{k_d k_t}} \quad (17e)$$

$$k_{pr} = k_p + k_{fm} \quad (17f)$$

$$R_{SM} = \frac{C_S}{(1+C_M)} \frac{M}{S} \approx \frac{C_S}{(1+C_M)} \frac{M_0}{S_0} \quad (17g)$$

$$R_{MM} = \frac{k_{fm}}{k_{pr}} = R_M \quad (17h)$$

$$C_S = \frac{k_{fs}}{k_p} \quad (17i)$$

$$C_M = \frac{k_{fm}}{k_p} \quad (17j)$$

$$R_S = \frac{k_{fs}}{k_{pr}} \quad (17k)$$

In conjunction with Eqs.11 (a - c), the values of λ_0 , λ_1 , λ_2 , μ_0 , μ_1 , μ_2 for each of the reaction conditions 1a -10d (Table 12) can be estimated

3.13. Monomer Conversion Model

Considering the elementary steps shown below, we have:

Initiation:



$$r_{R^\bullet} = 2fk_d C_I \quad (18a)$$

Chain Initiation:



$$r_{R^\bullet} = k_{CI} C_M C_{R^\bullet} \quad (20)$$

Propagation:



Termination by Combination:



Termination by Disproportionation:



Table 12: Estimation of live and dead moments at various reaction conditions

S/N	Reaction time (mins)	Initiator conc. (mol/L)	Temperature (K)
1a.	10	0.0825	363
1b.	10	0.0620	363
1c.	10	0.0413	363
1d.	10	0.0206	363
2a.	10	0.0825	333
2b.	10	0.0620	333
2c.	10	0.0413	333
2d.	10	0.0206	333
3a.	20	0.0825	363
3b.	20	0.0620	363
3c.	20	0.0413	363
3d.	20	0.0206	363
4a.	20	0.0825	333
4b.	20	0.0620	333
4c.	20	0.0413	333
4d.	20	0.0206	333
5a.	30	0.0825	363
5b.	30	0.0620	363
5c.	30	0.0413	363
5d.	30	0.0206	363
6a.	30	0.0825	333
6b.	30	0.0620	333
6c.	30	0.0413	333
6d.	30	0.0206	333
7a.	40	0.0825	363
7b.	40	0.0620	363
7c.	40	0.0413	363
7d.	40	0.0206	363
8a.	40	0.0825	333
8b.	40	0.0620	333
8c.	40	0.0413	333
8d.	40	0.0206	333
9a.	50	0.0825	363

9b.	50	0.0620	363
9c.	50	0.0413	363
9d.	50	0.0206	363
10a.	50	0.0825	333
10b.	50	0.0620	333
10c.	50	0.0413	333
10d.	50	0.0206	333

\

The following assumptions were made;

I. Steady State Approximation for radical concentration.

II. Rate of initiation is equal to the rate of termination.

Mass balance on the generated radicals gives:

$$r_{R^{\bullet}} = 2fk_d C_I \quad k_{CI} C_M C_{R^{\bullet}} \approx 0 \quad (24)$$

$$C_{R^{\bullet}} = \frac{2fk_d C_I}{k_{CI} C_M} \quad (25)$$

$$\text{From Eq. (21), } R_P = \frac{dC_M}{dt} = k_p C_P^{\bullet} C_M \quad (26)$$

$$\text{Considering } R_I = R_t \quad (27)$$

$$2fk_d C_I = 2k_t C_P^{\bullet 2} \quad (28)$$

The factor 2 arises from the fact that at each incidence of termination reaction, two radicals disappear.

$$C_P^{\bullet 2} = \frac{2fk_d C_I}{2k_t} \quad (29)$$

$$C_P^{\bullet} = \sqrt{\frac{fk_d C_I}{k_t}} \quad (30)$$

Substituting Eq.(30) in Eq.(26)

$$R_P = \frac{dC_M}{dt} = k_p \left(\frac{fk_d}{k_t} \right)^{\frac{1}{2}} C_I^{\frac{1}{2}} C_M \quad (31)$$

From Eq. (18):

$$\frac{dC_I}{dt} = k_d C_I \quad (32)$$

Separating the variables and integrating both sides, we have:

$$\frac{dc_I}{c_I} = -k_d dt \quad (33)$$

$$\ln C_I = -k_d t, \text{ putting limit from } C_{I_0} \text{ to } C_I \quad (34)$$

$$\frac{C_I}{C_{I_0}} = e^{-k_d t} \quad (35)$$

$$C_I = C_{I_0} e^{-k_d t} \quad (36)$$

Substituting Eq. (36) in Eq.(31)

$$\frac{dC_M}{dt} = k_p \left(\frac{fk_d}{k_t} \right)^{\frac{1}{2}} (C_{I_0} e^{-k_d t})^{\frac{1}{2}} C_M \quad (37)$$

Assuming $k_\alpha =$

$$k_p \left(\frac{fk_d}{k_t} \right)^{\frac{1}{2}} \quad (38)$$

$$\frac{dC_M}{dt} = k_\alpha (C_{I_0})^{\frac{1}{2}} e^{-\frac{k_d t}{2}} C_M \quad (39)$$

$$\frac{dC_M}{C_M} = k_\alpha (C_{I_0})^{\frac{1}{2}} e^{-\frac{k_d t}{2}} dt \quad (40)$$

Initial conditions:

$$C_M = C_{M_0} \quad : t = 0 \text{ and defining}$$

$$x = \frac{M_0 - M}{M_0} = \left[1 - \frac{M}{M_0} \right] \quad (41)$$

For the Left Hand Side (L.H.S) of Eq. (40) :

$\ln C_M$ taking limit from C_{M_0} to C_M , we have

$$\ln C_M - \ln C_{M_0} \quad (42)$$

$$\ln C_M + \ln C_{M_0} \quad (43)$$

$$\ln C_{M_0} - \ln C_M = \ln \frac{C_{M_0}}{C_M} \quad (44)$$

$$\text{But } x = 1 - \frac{C_M}{C_{M_0}} \quad (45)$$

$$\text{i.e. } \frac{C_M}{C_{M_0}} = 1 - x \quad (46)$$

$$\ln \frac{C_M}{C_{M_0}} = \ln \frac{C_{M_0}}{C_M} = -\ln(1 - x) \quad (47)$$

Integrating R.H.S of Eq. (40) , we have:

$$\frac{k_\alpha (C_{I_0})^{\frac{1}{2}} e^{-\frac{k_d t}{2}}}{-\frac{k_d}{2}} \quad (48)$$

$$-\frac{2}{k_d} k_\alpha (C_{I_0})^{\frac{1}{2}} e^{-\frac{k_d t}{2}} \quad (49)$$

Putting limits from $t = 0$ to $t = t$

$$-\frac{2}{k_d} k_\alpha (C_{I_0})^{\frac{1}{2}} e^{-\frac{k_d t}{2}} - \left[-\frac{2}{k_d} k_\alpha (C_{I_0})^{\frac{1}{2}} \right] \quad (50)$$

$$\frac{2}{k_d} k_\alpha (C_{I_0})^{\frac{1}{2}} - \frac{2}{k_d} k_\alpha (C_{I_0})^{\frac{1}{2}} e^{-\frac{k_d t}{2}} \quad (51)$$

$$\frac{2}{k_d} k_\alpha (C_{I_0})^{\frac{1}{2}} \left[1 - e^{-\frac{k_d t}{2}} \right] \quad (52)$$

Now equating Eq. (48) and Eq.(52):

$$\ln(1 - x) = \frac{2}{k_d} k_\alpha (C_{I_0})^{\frac{1}{2}} \left[1 - e^{-\frac{k_d t}{2}} \right] \quad (53)$$

$$\ln(1 - x) = k_\beta \left[1 - e^{-\frac{k_d t}{2}} \right] \quad (54)$$

OR

$$\ln(1 - x) = k_\beta \left[e^{-\frac{k_d t}{2}} - 1 \right] \quad (55)$$

$$\text{where } k_\beta = \frac{2}{k_d} k_\alpha (C_{I_0})^{\frac{1}{2}} \quad (56)$$

$$k_\alpha = k_p \left(\frac{f k_d}{k_t} \right)^{\frac{1}{2}} \quad (57)$$

Westerhout *et al.*, (1997) in their report concluded that all published polymerization models are limited to narrow conversion ranges. One common trend observed which may further support their opinion in modeling polymerization processes is that the tasking direct determination of kinetic parameters have made researchers to rely frequently on kinetic parameters taken from literature values in which experimental conditions may be considerably different. Wu *et al.*, (1982), in their intensive report on batch polymerization of styrene stated a feature of free radical polymerization in bulk called the gel or Trommsdorff-Norrish effect where the rate of reaction increases with an increase in conversion instead of decreasing as monomer is consumed. They attributed the gel effect to a decrease in the rate of termination and consequently an increase in the styrene monomer macro-radical concentration. They further related the decrease in termination rate to the restricted diffusion of macro-radicals in the polymerizing system of high viscosity. Choe (2003) in his study of estimation of diffusion controlled reaction parameters in photo-initiated polymerization of dimethacrylate macromonomers, similarly observed that the reaction became diffusion controlled due to the restricted mobility of the dimethacrylate macromonomers. Kee and Kyu (1988) observed that the gel effect in styrene polymerization is not as strong as in other vinyl monomer polymerization especially methylmethacrylate (MMA) polymerization. Still, the gel effect is not quite negligible at high conversion or low solvent volume fraction. The approach of Kee and Kyu (1988) was adopted in this study to correct the earlier monomer conversion model. Herein, the gel effect ($g(t)$) correlation suggested by Friis and Hamielec (1976) for bulk styrene polymerization was used and modified for solution polymerization as demonstrated by Hamer *et al.*, (1981).

$$g(t) = \frac{k_t}{k_{t0}} = \exp[-2(Bx + Cx^2 + Dx^3)] \quad (58)$$

where x and k_{to} denote the monomer conversion and the terminal rate constants at zero monomer conversion.

$$B = 2.57 - 5.05 \times 10^{-3} T(K) \quad (59)$$

$$C = 9.56 - 1.76 \times 10^{-2} T(K) \quad (60)$$

$$D = -3.03 - 7.85 \times 10^{-3} T(K) \quad (61)$$

The constants B, C and D were from the work of Hui and Hamielec(1972) to correct the gel effect and are used till today in majority of studies of vinyl monomer polymerization.

Incorporating the gel effect into the earlier model, we have :

$$\ln(1-x) = k_{\beta} [e^{\frac{-k_d t}{2}} - 1] + g(t) \quad (62)$$

The incorporation of the gel effect is intended to improve the model accuracy though also increasing the model complexity.

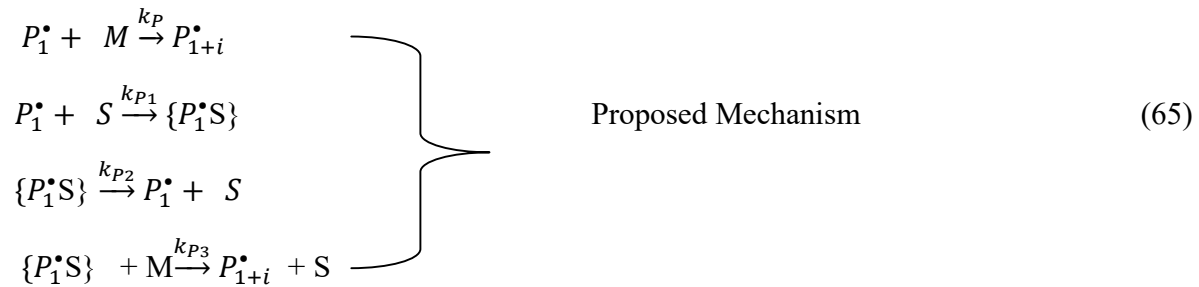
$$\ln \frac{1}{1-x} = k_{\beta} [e^{\frac{-k_d t}{2}} - 1] + e^{-2(Bx + Cx^2 + Dx^3)} \quad (63)$$

$$\ln \frac{1}{1-x} = k_{\beta} e^{\frac{-k_d t}{2}} - k_{\beta} + e^{-2(Bx + Cx^2 + Dx^3)} \quad (64)$$

3.14 Kinetics of Solvents Effects (KSEs)

Previous studies such as Schleicher and Scurto (2009) made claim that solvents are not actually spectators in the free radical reaction or just to provide an inert medium for heat dissipation but influence in a way the propagation step of the reaction. The different conversions obtained from the solvents used are an indication that their interaction in the reaction medium is significant. It was observed that the styrene conversion and reaction rates tend to be a function of the solvent media especially the polarity or other intermolecular forces which may vary from polarization

and dipole interactions up to stronger hydrogen bond. All these are indications of formation of further complexes either radical-solvent complexes or monomer - solvent complexes. These earlier observations made us to propose a sub-reaction kinetic scheme (Eq.65) within the reaction propagation step to kinetically determine the fate of the solvent.



Using the steady state approximation:

$$\frac{d\{P_1^\bullet S\}}{dt} = 0 = k_{p1}[P_1^\bullet][S] - k_{p2}[\{P_1^\bullet S\}] - k_{p3}[\{P_1^\bullet S\}][M] \quad (66)$$

$$\frac{d\{P_1^\bullet S\}}{dt} = 0 = k_{p1}[P_1^\bullet][S] - [\{P_1^\bullet S\}][k_{p2} + [k_{p3}M]] \quad (67)$$

$$[\{P_1^\bullet S\}] = \frac{k_{p1}[P_1^\bullet][S]}{k_{p2} + [k_{p3}M]} \quad (68)$$

$$[P_1^\bullet] = \frac{[\{P_1^\bullet S\}][k_{p2} + [k_{p3}M]]}{k_{p1}[S]} \quad (69)$$

$k_{p,mean} = f_f k_p + f_c k_{p3}$, where f_f and f_c are the weight fractions of the free chains and complexed chains, respectively.

$$f_f = \frac{\frac{[\{P_1^\bullet S\}][k_{p2} + [k_{p3}M]]}{k_{p1}[S]}}{\frac{[\{P_1^\bullet S\}][k_{p2} + [k_{p3}M]]}{k_{p1}[S]} + \frac{k_{p1}[P_1^\bullet][S]}{k_{p2} + [k_{p3}M]}} \quad (70)$$

$$f_c = \frac{\frac{k_{P_1}[P_1^\bullet][S]}{k_{P_2}+[k_{P_3}M]}}{\frac{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]}{k_{P_1}[S]} + \frac{k_{P_1}[P_1^\bullet][S]}{k_{P_2}+[k_{P_3}M]}} \quad (71)$$

Substituting Eq.70 and 71 in $k_{p,mean}$ equation

$$k_{p,mean} = \frac{\frac{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]}{k_{P_1}[S]} k_p}{\frac{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]}{k_{P_1}[S]} + \frac{k_{P_1}[P_1^\bullet][S]}{k_{P_2}+[k_{P_3}M]}} + \frac{\frac{k_{P_1}[P_1^\bullet][S]}{k_{P_2}+[k_{P_3}M]} k_{p3}}{\frac{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]}{k_{P_1}[S]} + \frac{k_{P_1}[P_1^\bullet][S]}{k_{P_2}+[k_{P_3}M]}} \quad (72)$$

$$k_{p,mean} = \frac{\frac{k_{P_2}+[k_{P_3}M]\{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]k_p+k_{P_1}[S]k_{P_1}[P_1^\bullet][S]k_{p2}\}}{k_{P_1}[S](k_{P_2}+[k_{P_3}M])}}{\frac{\{k_{P_2}+[k_{P_3}M]\}\{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]k_p+k_{P_1}[S]k_{P_1}[P_1^\bullet][S]k_{p2}\}}{k_{P_1}[S](k_{P_2}+[k_{P_3}M])}}} \quad (73)$$

$$k_{p,mean} =$$

$$\frac{k_{P_2}+[k_{P_3}M]\{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]k_p+k_{P_1}[S]k_{P_1}[P_1^\bullet][S]k_{p3}\}}{(k_{P_2}+[k_{P_3}M])\{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]+k_{P_1}[S]k_{P_1}[P_1^\bullet][S]\}+(k_{P_2}+[k_{P_3}M])\{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]+k_{P_1}[S]k_{P_1}[P_1^\bullet][S]\}} \quad (74)$$

$$k_{p,mean} = \frac{(k_{P_2}+[k_{P_3}M])\{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]k_p+k_{P_1}[S]k_{P_1}[P_1^\bullet][S]k_{p3}\}}{(k_{P_2}+[k_{P_3}M])\{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]+k_{P_1}[S]k_{P_1}[P_1^\bullet][S]\}} \quad (75)$$

$$k_{p,mean} = \frac{k_p + \frac{k_{P_1}[S]k_{P_1}[P_1^\bullet][S]k_{p3}}{(k_{P_2}+[k_{P_3}M])\{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]\}}}{1 + \frac{k_{P_1}[S]k_{P_1}[P_1^\bullet][S]}{(k_{P_2}+[k_{P_3}M])\{[\{P_1^\bullet S\}][k_{P_2}+[k_{P_3}M]]\}}} \quad (76)$$

$$k_{p,mean} = \frac{k_p + \frac{k_{P_1}[S]k_{p3}}{(k_{P_2}+[k_{P_3}M])}}{1 + \frac{k_{P_1}[S]}{(k_{P_2}+[k_{P_3}M])}} \quad (77)$$

If we assume that $k_{P_2} \gg [k_{P_3}M]$:

$$k_{p,mean} \approx k_p + \frac{k_{p1}[S]k_{p3}}{k_{p2}} \quad (78)$$

If $k_{p2} \ll [k_{p3}M]$:

$$k_{p,mean} \approx k_p + \frac{k_{p1}[S]}{[M]} \quad (79)$$

Eqs.77 - 78 clumped both the solvent and monomer concentration together. This undoubtedly is an indication that the interaction between the monomer and the solvent is a strong driving force for the reaction. We suspect varied energetic reaction pathway requirement for the solvents. This requirement may be based on nature of the complex formed (strong or weak) as they may modify the reactivity of the styrene monomer.

3.15. Process Optimization using Response Surface Methodology (RSM) and Statistical Analysis

Earlier studies in the course of this research have identified acetone as a good and proper solvent for the styrene polymerization. Polystyrene samples were therefore prepared via solution polymerization of styrene using acetone as solvent and benzoyl peroxide (BPO) as initiator. The variables studied were the reaction temperature (X_1), initiator concentration (X_2), and reaction time (X_3). All variables and their respective range were chosen as shown in Table 13 on the basis of preliminary studies of this polymerization system. A five-level-three-factor central composite design (CCD) was employed, requiring 20 experimental runs (calculated based on Eq. (80) which consist of 8 factorial runs, 6 axial runs and 6 replicates runs at the centre.

$$N = 2^{n^*} + 2n^* + N_c \quad (80)$$

where N is the total experimental runs, n^* is the number of variables and N_c is the centre point replication.

Table 13: Experimental variables and their coded levels for central composite design

Variables	Variables	Units	Coded variables level				
			-X	-1	0	1	X
Temperature	X_1	°C	39.55	60	90	120	140.45
Initiator Conc.	X_2	mol/l	0.0304	0.0515	0.0825	0.1135	0.1346
Reaction Time	X_3	mins	16.36	30	50	70	83.64

The α -value for this design was fixed at 1 (face-centered), and the response for this experiment was the percent monomer conversion (Y). The response was used to develop an empirical model that correlated the response to the three process variables using a second-degree polynomial as shown in Eq. (81).

$$Y = b_o + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_{ii} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} X_i X_j \quad (81)$$

where Y is the predicted response, b_o is a constant coefficient, b_i is a linear coefficient, b_{ii} is the quadratic equation, b_{ij} is an interaction coefficient, and X_i and X_j are the coded values of the polymerization variables. Table 14 (standard experimentation matrix) shows the run order, experimental design and the observed response (% monomer conversion) for the three variables and 20 experimental runs generated. Columns 2 to 4 represent the variable levels coded in the dimensionless coordinate while columns 5 to 7 represent the dimensional variable levels. Table 14 similarly shows the experimental values obtained for the response (column 8).

Table 14: Experimental design matrix for the preparation of the styrene polymerization

Run	Coded Factor			Actual Factor			% Conversion	
	X ₁	X ₂	X ₃	X ₁ (°C)	X ₂ (mol/l)	X ₃ (min)	Observed response	Predicted response
1	0	0	0	90	0.0825	50	47.46	48.23
2	0	0	0	90	0.0825	50	48.12	48.23
3	-1	-1	-1	60	0.0516	30	33.55	37.53
4	0	0	1.6818	90	0.0825	83.6359	48.34	50.53
5	0	0	0	90	0.0825	50	48.79	48.23
6	-1	1	-1	60	0.1135	30	45.92	48.44
7	0	1.68179	0	90	0.1346	50	57.84	58.40
8	-1	1	1	60	0.1135	70	44.37	45.16
9	1	1	-1	120	0.1135	30	76.82	76.41
10	-1.6818	0	0	39.546	0.0825	50	45.25	40.59
11	-1	-1	1	60	0.0516	70	34.88	36.02
12	1	-1	1	120	0.0516	70	54.31	52.53
13	0	0	0	90	0.0825	50	49.00	48.23
14	1	-1	-1	120	0.0516	30	55.19	55.14
15	1	1	1	120	0.1135	70	75.28	72.04
16	0	0	0	90	0.0825	50	47.24	48.23
17	0	0	0	90	0.0825	50	48.57	48.23
18	0	0	-1.6818	90	0.0825	16.3641	58.72	55.48
19	0	-1.6818	0	90	0.0304	50	34.44	32.83
20	1.6818	0	0	140.454	0.0825	50	74.39	78.00

Design Expert software (MINITAB 16.1) was used for RSM regression analysis and optimization of monomer conversion data with input parameters. The statistical testing of the model, which includes linear, quadratic and interaction coefficient, was performed by ANOVA analysis with F-test to obtain the empirical correlation between input and output parameters. To examine the goodness of fit of the model, each term of model is tested statistically to confirm the significance of F - values with $p \leq 0.05$. The influence of the term (process parameter) will be significant if the value of the critical level $p < 0.05$ (Box *et al.*, 2005). The values of R^2 (Coefficient of Determination), adjusted R^2 , and predicted R^2 , lack of fit and adequate precision of models are obtained to check the quality of the suggested polynomial. The response surface plot and contour plot were drawn drawn to visualize the input-output relationships.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

In this chapter, the results of our experimental study were presented and the discussion of the different aspects of the results. Firstly, the effect of solvent and initiator on monomer conversion against reaction time was discussed in Subsection (4.1). The possibility of synergy between acetone and chloroform as co-solvent was then explored. In the second Subsection (4.2), the effect of solvent polarity on monomer conversion using a single parameter, the dielectric constant, and then a multiparameter correlation through the linear solvation energy relationship was discussed. Polymerization in green solvents was presented in the third Subsection (4.3-4.12), with analyses leading to choice of a good solvent for solution polymerization of styrene. Also presented were statistical analysis of experimental data, results of the kinetic modeling and optimization studies using the RSM. In the last section, we present analyses of the synthesized PS.

4.1. Effect of Nature of Solvent and Initiator on Styrene Monomer Conversion

Four solvents, acetone, benzene, chloroform and toluene on the basis of different polarities were initially investigated in the reaction to explore monomer, solvent, initiator and polymer compatibility. Tables 43 and 44 (Appendix A) show the polymer yield and polymerization rate in various solvents using BPO and BPO Blend respectively with respect to the specified reaction conditions (120 °C, 5 mL of Styrene monomer, $[M]_0 = 8.612 \text{ mol/L}$, Stirring Rate of 500 rpm and 0.1g of Initiators). Polymerization rates were calculated from the molar conversion of styrene with respect to polymerization time as described by Eqs.(1-4).

Figure 6 and Figure 7 exhibited similar behaviour for all the solvents used. The curves showed apparently that conversion vary markedly with the kind of solvent used. Two stages were observed here namely, the acceleration stage and stationary stage which were more pronounced in chloroform and Benzene and also occurred at roughly reaction time of 10 minutes and 20-50 minutes respectively for all the solvents used irrespective of the initiator.

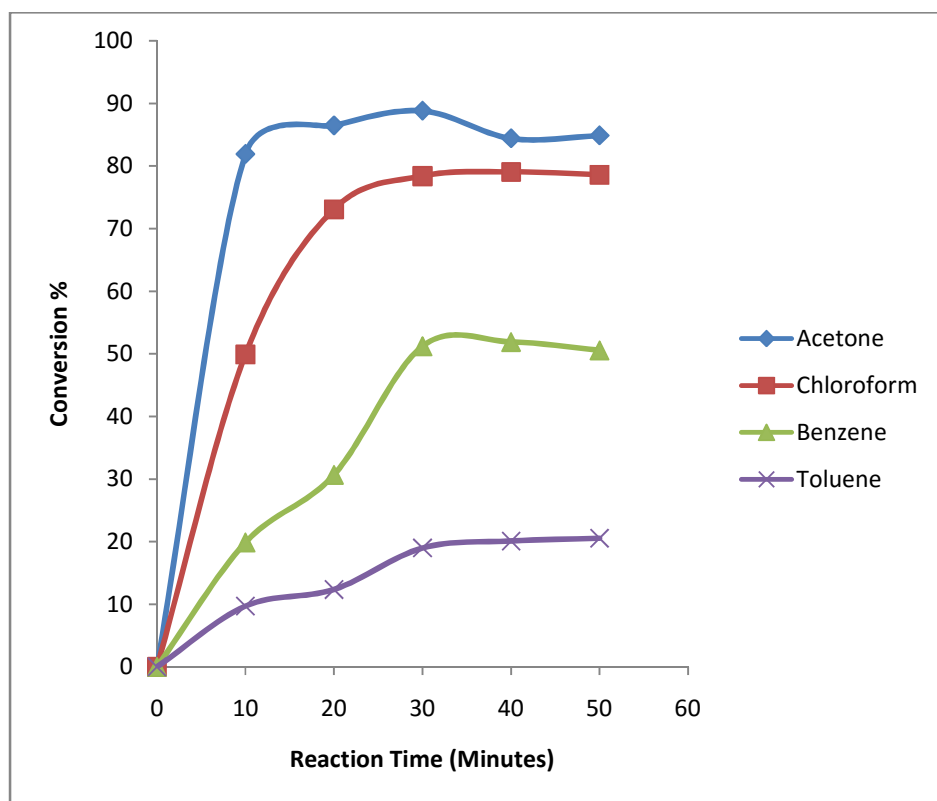


Figure 6: Variation of % conversion with reaction time at $\frac{\text{Styrene}}{\text{Solvent}} = 1$, BPO as initiator

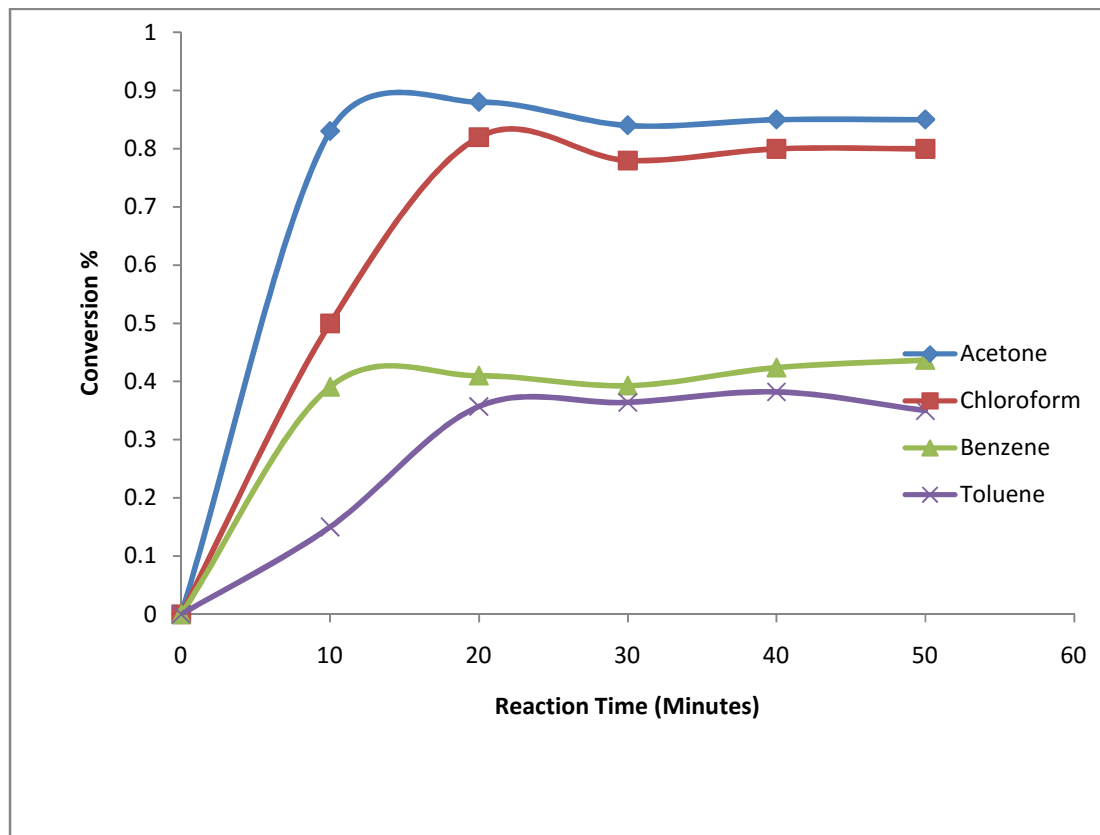


Figure 7 : Variation of % conversion with reaction time at $\frac{\text{Styrene}}{\text{Solvent}} = 1$, BPO Blend as initiator.

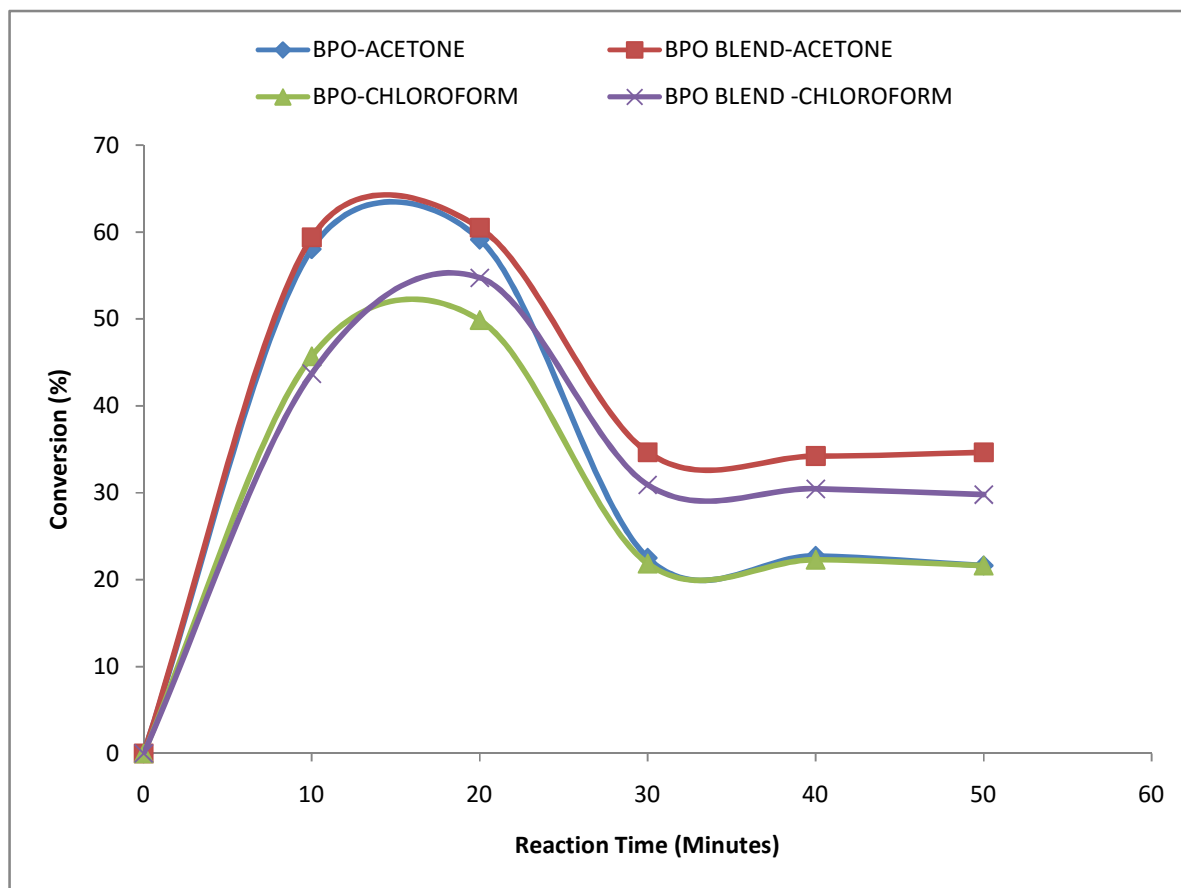


Figure 8: Variation of % Conversion with reaction time at $\frac{\text{Styrene}}{\text{Solvent}} = 0.33$

Figure 8 introduced the decelerating stage into the profile in addition to the earlier trends. The decrease in concentration of the monomer with time was suspected to be responsible for the decelerating stage. The conversion of monomer to polymer was determined by direct stopping of the polymerization reaction, isolating and weighing the resulting polymer. The handling of the polymer during precipitation, filtration and drying may lead to losses.

In all, highest conversions were observed in acetone, a polar solvent, irrespective of the type of initiator used and solvents volume. Similarly, conversions were found to decrease with decrease in styrene /solvent ratio. Toluene recorded the least conversion in all cases. As earlier remarked,

reported literature on various aspects of solution polymerization of styrene revealed that toluene is the common solvent used (Goto and Fukuda, 1999; Ozkam *et al.*, 1998; 2009; Altinten *et al.*, 2003; 2006; 2008; Alpbaz *et al.*, 2008; Ghasem *et al.*, 2007; Vicevic *et al.*, 2008; Noor *et al.*, 2010; Novakovic *et al.*, 2003; Hosen and Hussein, 2012; Hosen *et al.*, 2011a; 2011b; 2014a; 2014b; Mohammadi *et al.*, 2014). For other solvents investigated, the polymerization rate increased due to the diffusion controlled termination process at the initial stage of the reaction except for toluene was suspected. As a result, polymerizations in toluene especially at early stage tends to follow the classical free radical polymerization kinetics which most researchers find interesting especially for academic purpose.

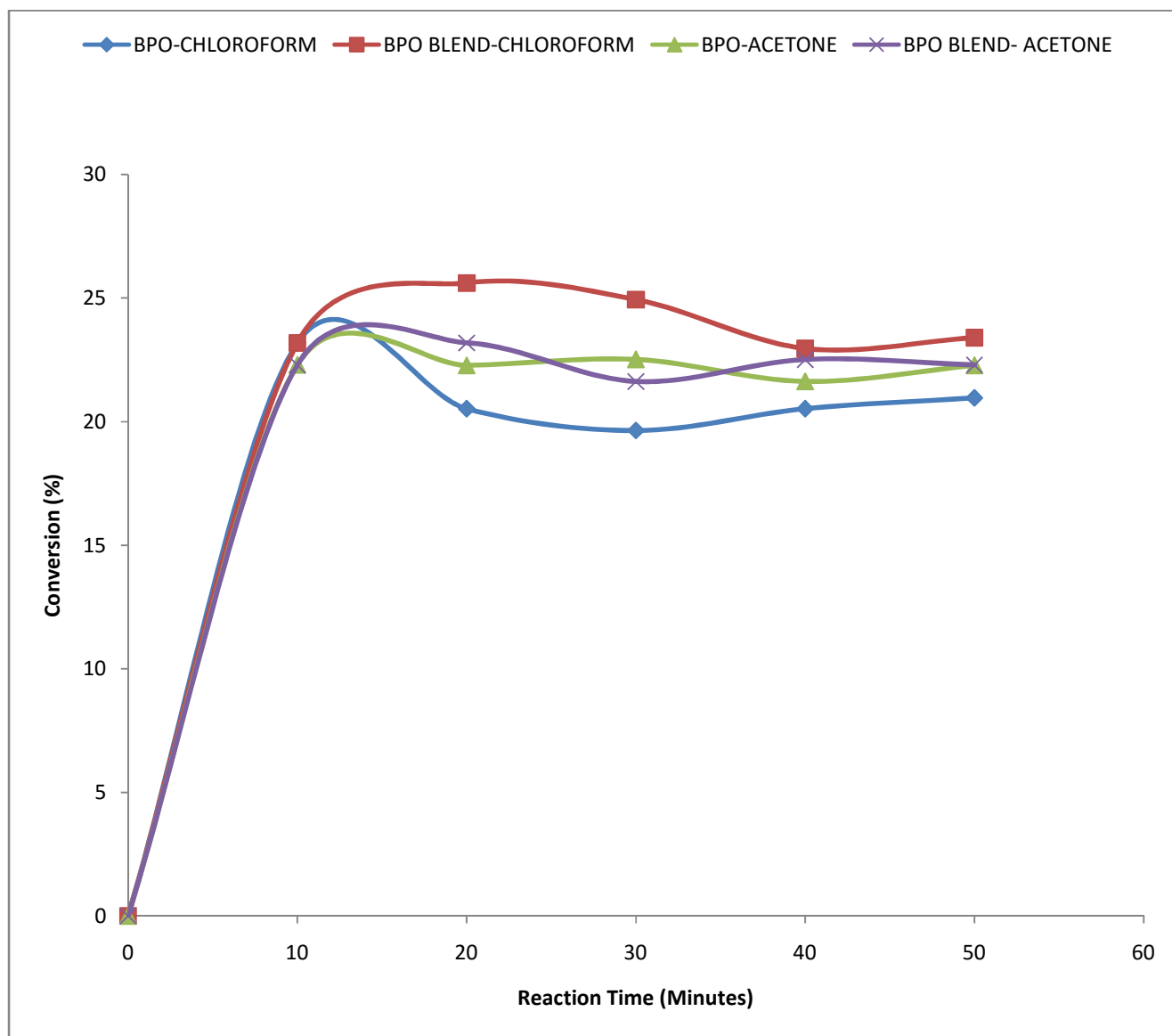


Figure 9: Variation of % Conversion with reaction time at $\frac{\text{Styrene}}{\text{Solvent}} = 0.25$

Figure 9 exhibits similar behaviour but with low conversion. The low conversion observed here is attributed to reduced radical formation for more diluted reaction mixtures. Chloroform also seems to give better conversion at high solvent volume.

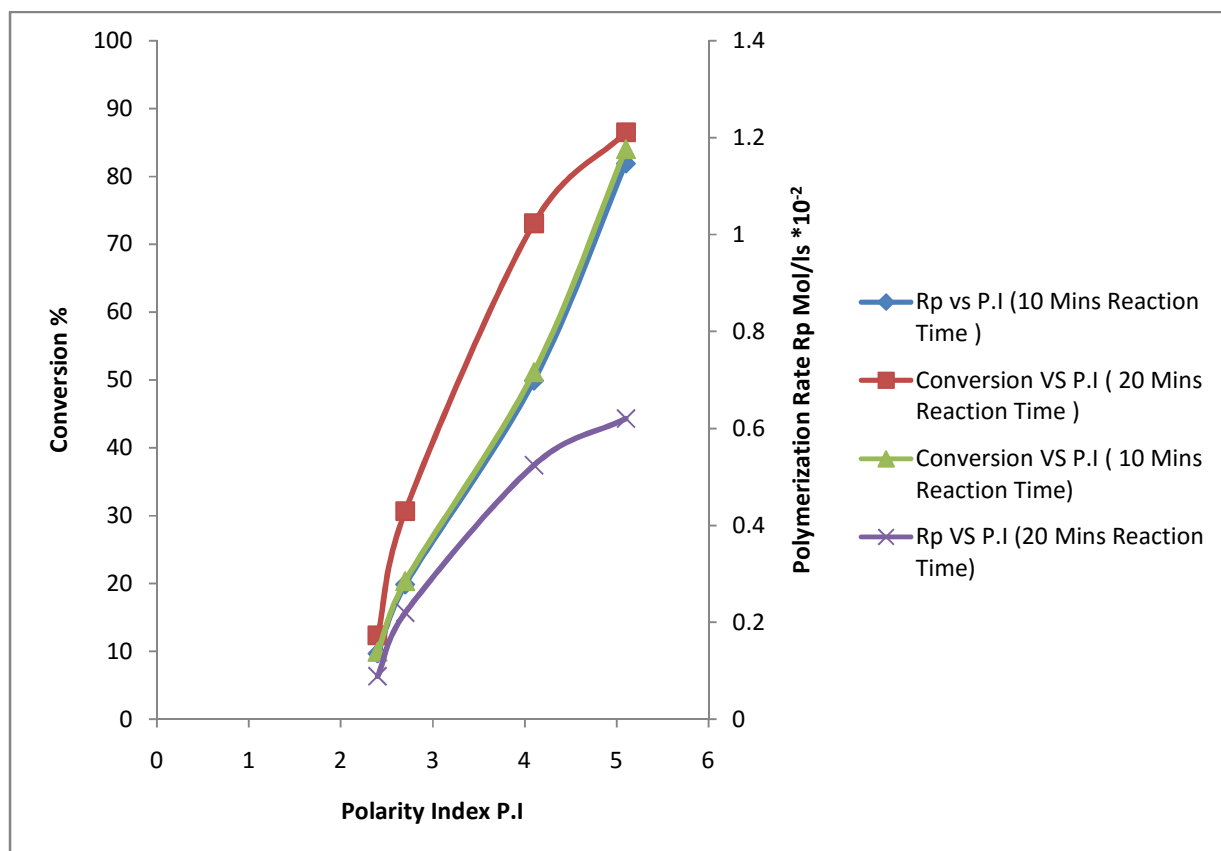


Figure 10: Variation of Polymerization rate (Rp) /Conversion Profile with Polarity Index (PI) using BPO

However, a relationship was established between the solvent properties, conversion and polymerization rate as shown in Figure 10. The higher the polarity index and di-electric constant of the solvents, the higher both the conversion and the polymerization rate. From our previous

control experiment, the styrene monomer and initiator are all needed for polymerization. However, Gao and Penlidis (1996) surprisingly cited experimental data from Hui and Hamielec (1972) which showed that monomer conversion for styrene thermal and self-initiation reached 40 % conversion after 5 hrs at 120 °C, and later 94 % after 30 hrs. One advantage identified from their work is the absence of initiator which on a credit side, reduces the production cost. BPO and its Blend, used in our study gave convincing account of their roles as initiators where we experienced polymer build up as early as 10 minutes of reaction time.

Figure 10 and Figure11 similarly exhibited almost similar profiles for the different reaction times. Initially, the conversion increased as the volume of the solvent increases but later decreased at higher volume of solvent. This change of behaviour was noted at about 5 to 10 ml of solvent. The reduced conversion observed is believed to be due to the reduced efficiency of the styrene polymerization at certain points. We have attributed the reduced efficiency to :

1. Dilution of the initiator
2. Chain transfer to solvent and
3. Reduced monomer concentration

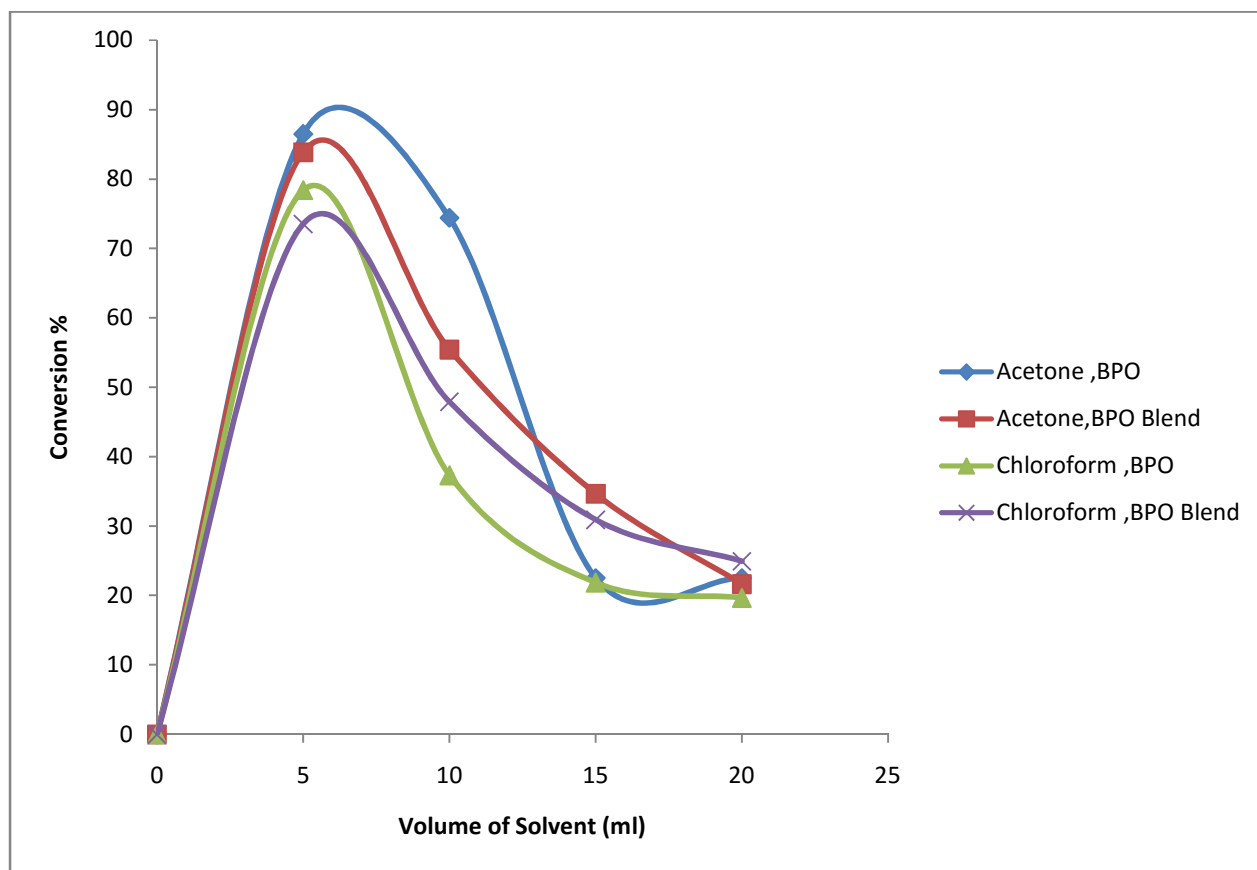


Figure 11: Variation of % conversion with volume of solvent at 30 minutes reaction time.

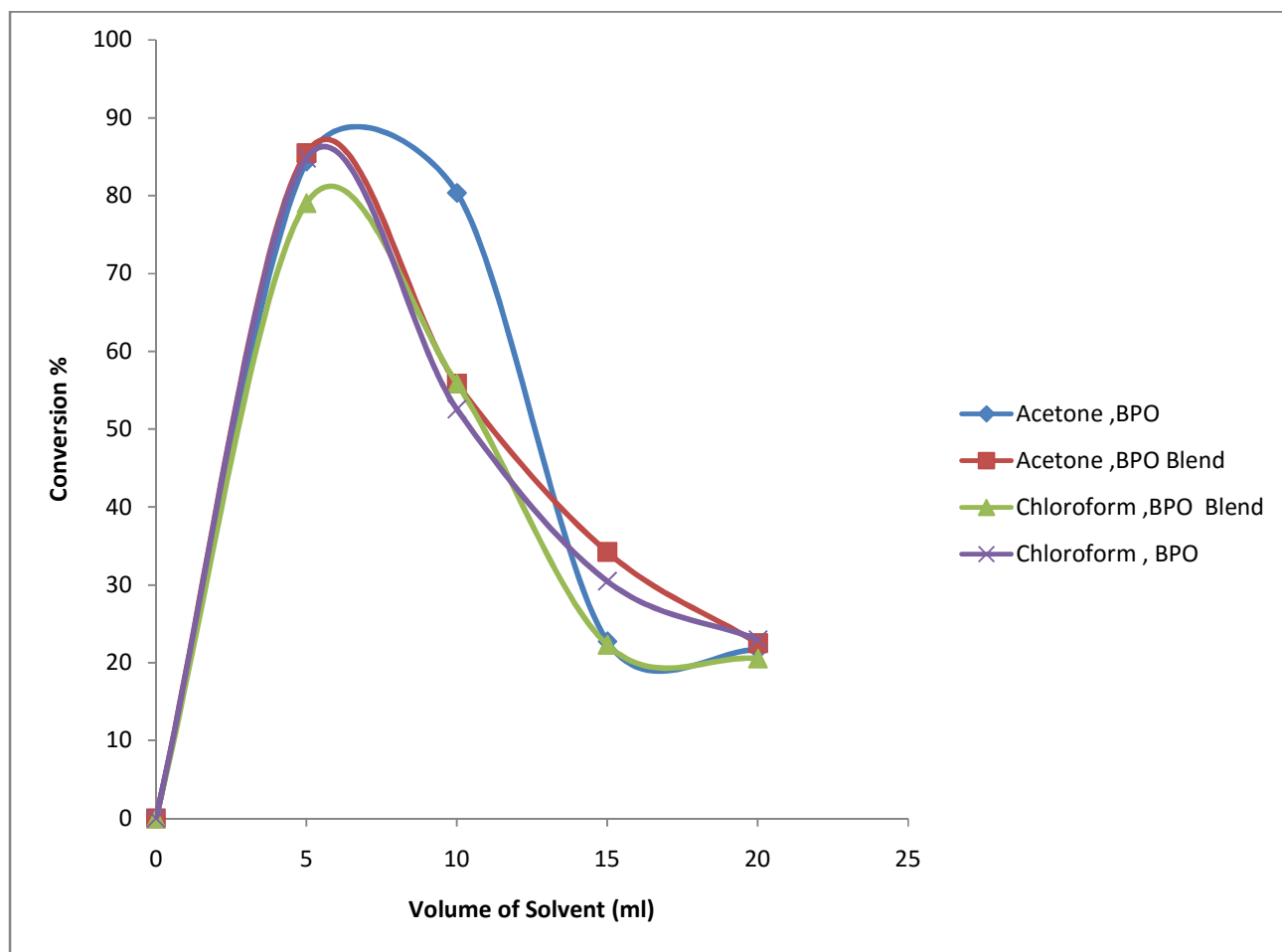


Figure 12: Variation of % Conversion with volume of solvent at 40 minutes reaction time

Tables 45 and 46 (Appendix B) show the polymer yield and polymerization rate in more polar solvents compared to those used in Table 43 and Table 44 (Appendix A) using BPO and BPO BLEND respectively with respect to the same reaction conditions.

Figures 13 and 14 show styrene conversion against reaction time for all the seven solvents at 120 °C using benzoyl peroxide and its blend with dicyclohexylphthalate, respectively. As shown in both figures, the nature of solvent highly influenced the monomer conversion. A radical solvent or radical monomer complex is likely to have been formed during the propagation step. Equation 65 suggests mechanism for the formation of the complex with growing polymer radical, while Eqs.66 through to 67 describe the dependency of the reaction propagation step on the solvent. The k_p values have been shown to increase by some factors (Eqs.78 and 79). This is consistent with earlier conclusions that k_p values in solution polymerization are higher than in bulk polymerization (Beuermann and Garcia, 2004). In Figure 13 at a reaction time of 20 min, the highest conversion of 85 % was obtained for acetone while the lowest conversion of 10 % was attained for toluene. Using toluene as solvent, monomer conversion of 20 % was attained at a reaction time of 40 min. Vicevic *et al.* (2008) carried out solution polymerization of styrene in a spinning disc reactor using toluene and benzoyl peroxide as solvent and initiator, respectively. They obtained monomer conversion of 20 % at a reaction time of 120 minutes and temperature of 75 °C. This is in agreement with the result of the present study. In Figure 14 using BPO blend initiator, all the solvents exhibit profile essentially similar to the pattern in Figure 13. However, toluene seems to have improved performance using blend initiator compared to BPO. For instance, at a reaction time of 40 minutes, polymerization using BPO blend initiator gave about 35 % conversion as against 20 % conversion achieved using BPO. This indicate some measure of

improved compatibility between toluene and BPO blend initiator suggesting the latter's affinity for solvents of low polarity.

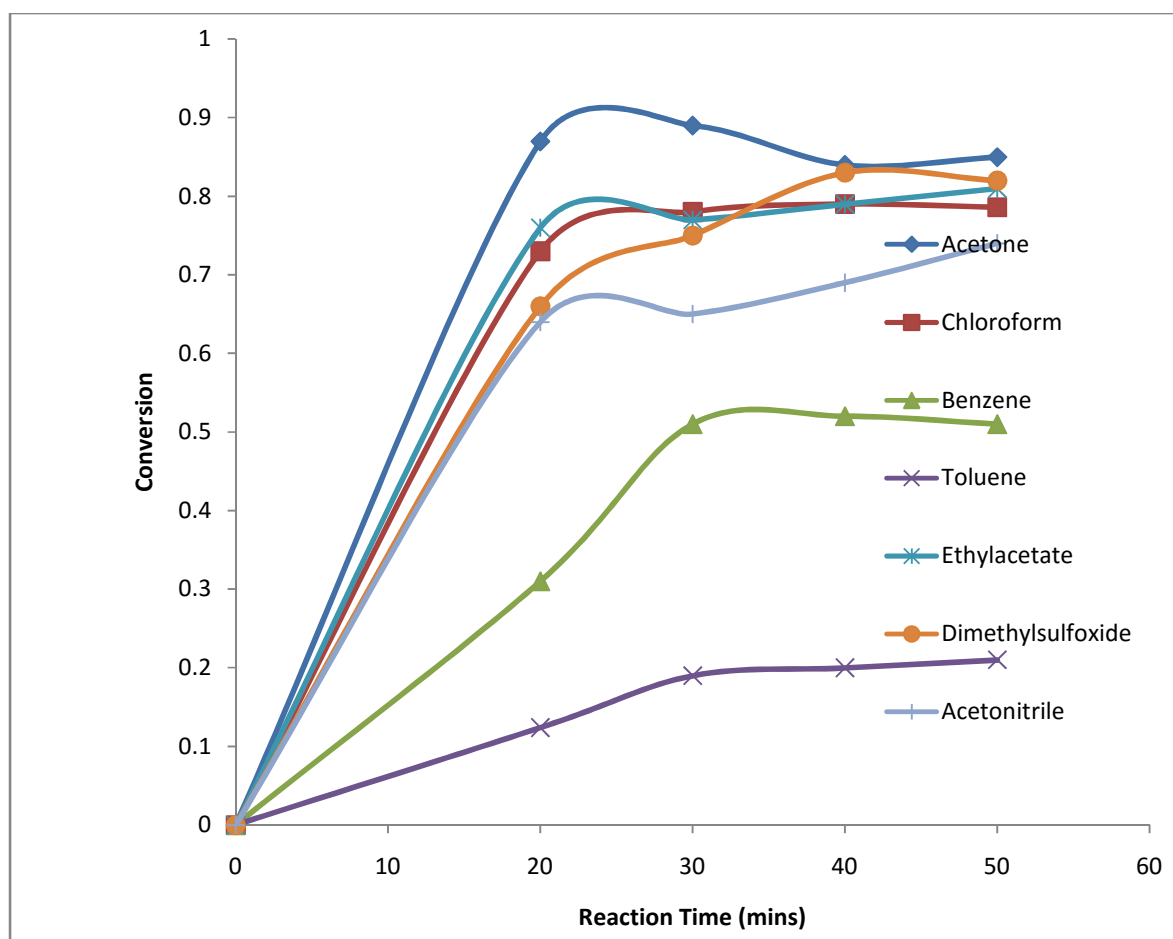


Figure 13: Variation of % conversion with reaction time in different solvent media at 120°C using BPO Initiator.

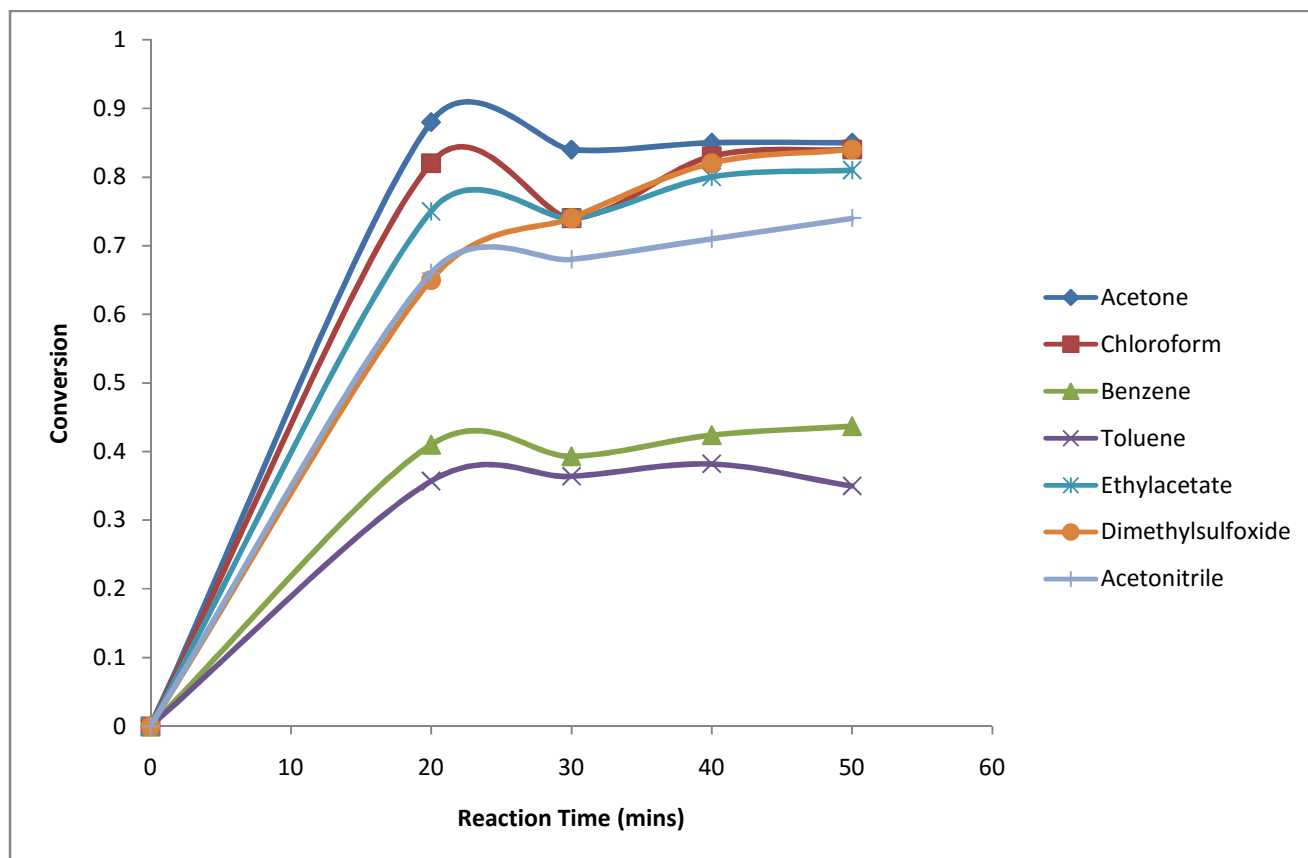


Figure 14: Variation of % conversion with reaction time in different solvent media at 120 °C using BPO Blend Initiator.

The order of monomer conversion in different media as depicted in Figure 13 and Figure 14 is as follows: acetone > ethylacetate > chloroform > DMSO > acetonitrile > benzene > toluene. However, the order of polarity for the solvents is as follows: DMSO > acetonitrile > acetone > ethylacetate > chloroform > benzene > toluene. It can be inferred that though degree of solvent polarity does influence the conversion, it is not the only contributory factor. In other studies, it is either that rate of reaction increased with polarity or it decreased with it. For example, Schleicher and Scurto (2009) reported, while studying the solvent effects in the synthesis of ionic liquid, that methanol, the most polar of the solvents used was found to be the slowest in terms of reaction rate. On the other hand, Horn and Matyjaszewski (2013) reported increasing rate constants of activation with increasing polarity in their study of solvent effects in atom transfer radical polymerization. In another study, Bahring *et al.*, (2014) used three different solvents on the basis of polarity to regulate the degree of polymerization (DPN) in weakly associated supramolecular oligomer, in the case of trichloromethane (Chloroform) and 1,2-dichloroethane, the degree of polymerization was found to be extremely low and did not show a meaningful increase as the total concentration of monomers was increased. On the other hand, in Methylcyclohexane, which was the most polar of all, strong concentration-dependent behaviour was observed with the DPN increasing with concentration. The present study reveals a different trend and requires further insightful analysis to properly situate our observations. Meanwhile, a minimum chain transfer to acetone within the operating conditions when compared to other solvents was suspected.

4.2. Rationalization of Solvent Effects

This section presents a rationalization of the observed solvent effect in Solution Polymerization of Styrene using a single Parameter and a Multiparameter analyses.

4.2.1. Single Parameter Assessment

Qualitative assessment of solvent effects can be made by correlating observed monomer conversion with the physical property of the solvent such as dielectric constant. Figures 15 and 16 show the effect of solvent polarity on the styrene polymerization initiated by both BPO and BPO blend, respectively. Di-electric constant is a rough measure of solvent polarity. The figures show clearly the overall effect of solvent polarity, in terms of the di-electric constant, on the styrene conversion. Each of the parabolic curve peaks at the dielectric constant value for acetone thereafter, a drop was observed. The curve was expected to peak for dimethyldisulfoxide (DMSO) been the most polar. As a result, increasing the solvent polarity to achieve higher conversion is not always quantitatively valid. This suggests interplay of other contributory factors especially at the molecular level in the styrene conversion.

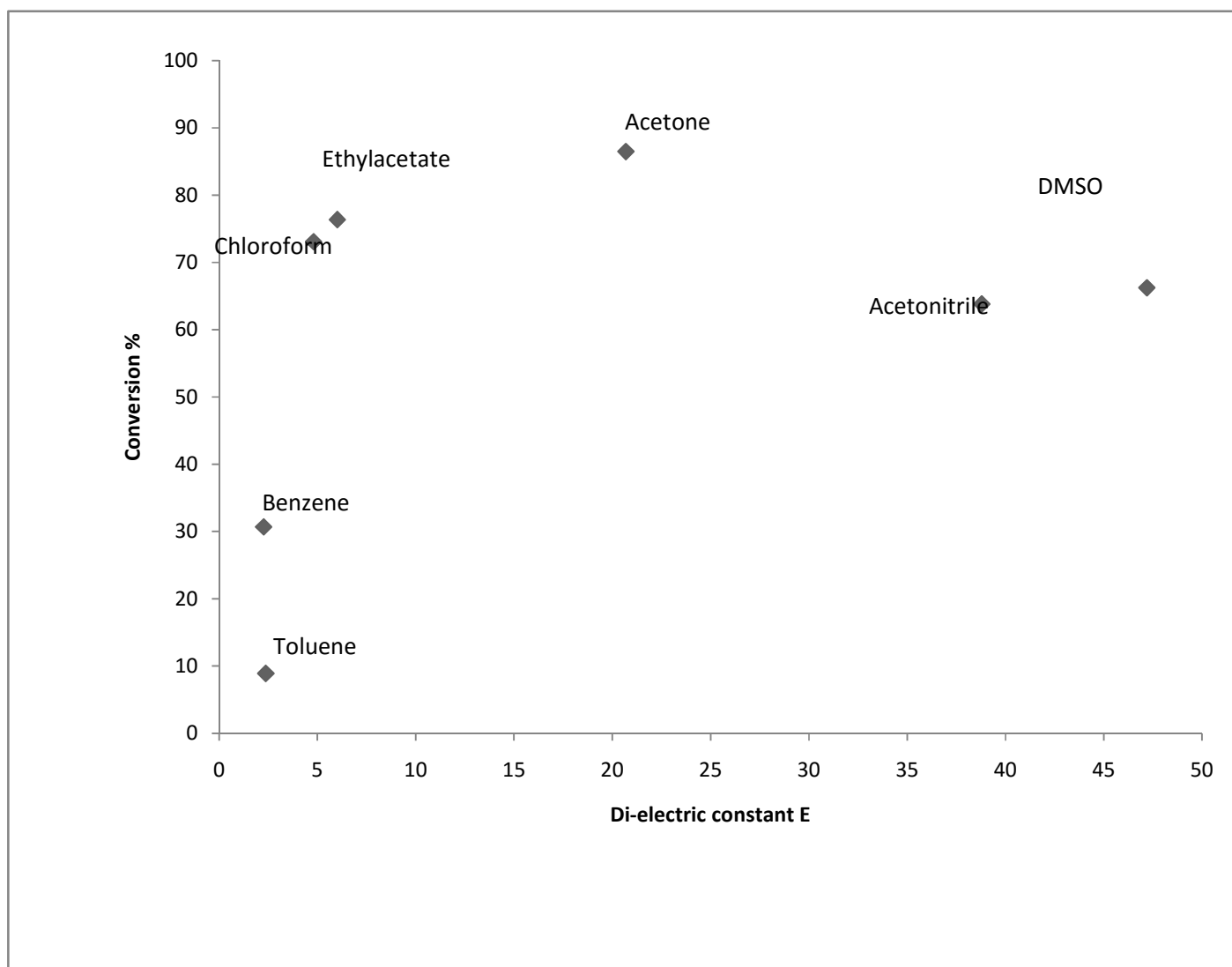


Figure 15: Variation of % Conversion with di-electric constant of solvents using BPO as initiator at 20 minutes reaction time

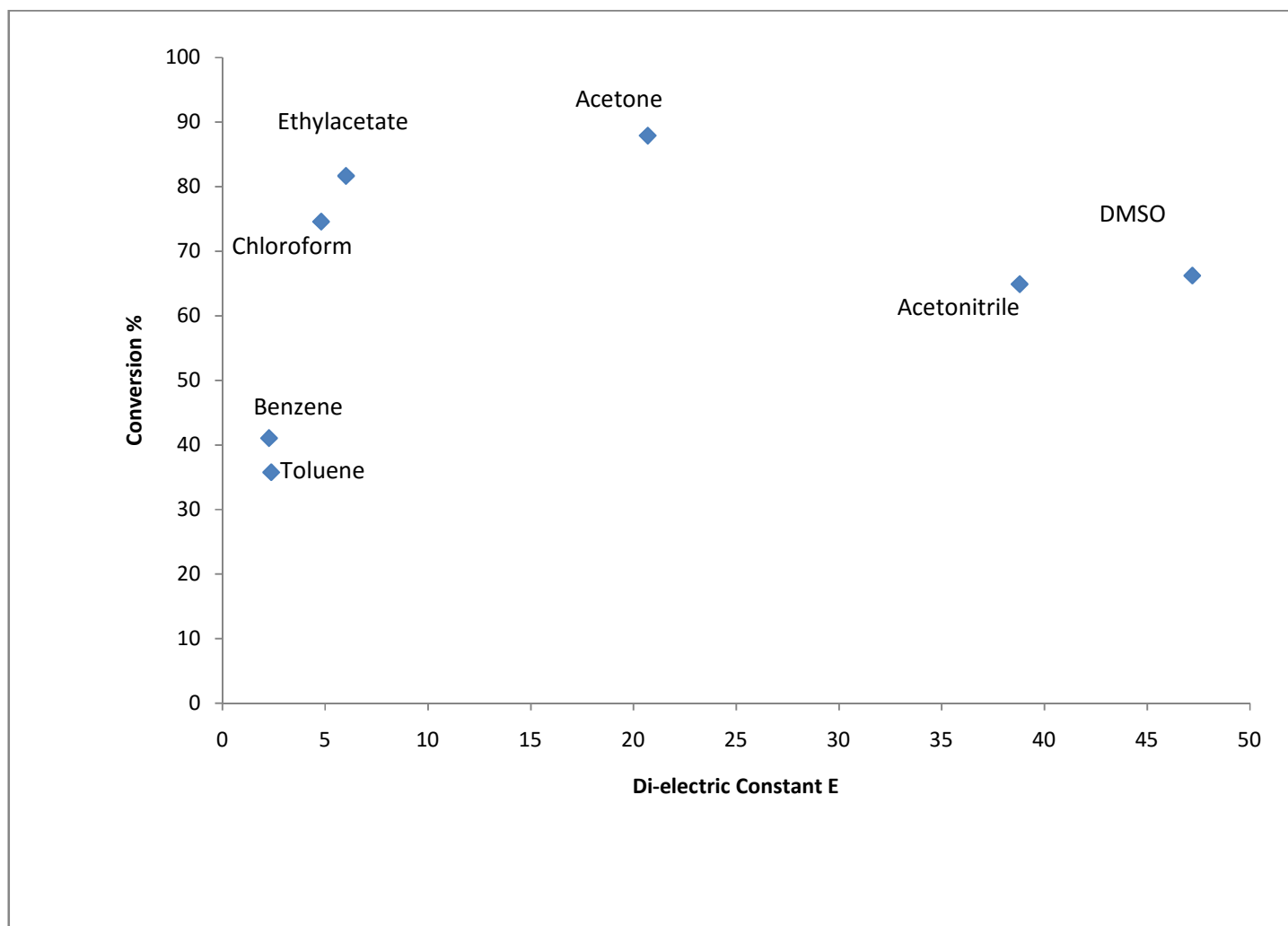


Figure 16: Variation of % conversion with di-electric constant of solvents using BPO Blend as initiator at 20 minutes reaction time

4.2.2. Multiparameter Assessment of Linear Solvation Energy Relationship

Solvation of a solute is an intricate process that can only be adequately described by a multiparameter relationship encompassing dipolar interactions, dispersion forces, ionic interaction, hydrogen bonding, or Lewis acid-base adduct formation (Horn and Matyjaszewski, 2013). Kamlet and Taft (KT) (1976a, 1976b) introduced a solvatochromic approach to solvent polarities that apportion the overall process of solvation into individual contributions or parameters. These parameters differentiate various aspect of polarity, viz; acidity (α), basicity (β), dipolarity /polarizability (π^*), etc. Acidity (α) is a measure of the solvent's ability to donate a proton in a solvent-to- solute hydrogen bond; Basicity(β) is a measure of the solvent's ability to accept a proton in a solvent-to-solute hydrogen bond and dipolarity(π^*) is a measure of the solvent's ability to stabilize a charge or dipole. The KT parameters of the solvent can be used to correlate and predict a solvation property of interest such as conversion, selectivity, rate constant, etc in different solvents using a Linear Solvation Energy Relationship (LSER). The LSER approach regresses parameters to correlate such solvation property with solvent-dependent physicochemical properties. For the peculiar pattern observed in our present study, monomer conversion is modeled by LSER of the form of Eq. (82):

$$X = b_0 + b_1 \pi^* + b_2 \alpha + b_3 \beta + b_4 E + b_5 n + b_7 E_T^N \quad (82)$$

where X = monomer conversion, π^* = dipolarity / polarizability , α = acidity , β = basicity , E = di-electric Constant, n = refractive Index , $E_T(30)$ = Dimroth-Reichardt electrophilicity, E_T^N = normalized E_T , b_0 is the constant for offset term, and b_1 - b_7 are coefficients for linear effects. The regressed coefficients indicate the magnitude and direction (positive or negative) the solvent parameters contribute to the styrene conversion.

4.3. Statistical Analysis of Experimental Data

The solvatochromic parameters of solvents used for the styrene polymerization are presented in Table 15, the results of the descriptive statistics and pearson correlation are presented in Tables 16-17: analysis of variance are presented in Tables 19 and 23, regression analysis coefficient are presented in Tables 20 and 24, excluded variables are presented in Tables 21 and 25, thermodynamics properties of the solvents are presented in Table 26, Physico-chemical and fatty acid composition of Biodiesel are presented in Tables 27 and 28, respectively and molecular weights of PS are presented in Tables 29-34, etc.

Table 15: Solvatochromic Parameters of Selected Solvents

Solvents	π^*	α	β	E	n [a]	E _T (30) kcal/mol	E _T ^N
ACETONE	0.71	0.08	0.48	20.70	1.3590	42.20	0.355
CHLOROFORM	0.58	0.44	0.00	4.81	1.4429	39.09	0.259
BENZENE	0.59	0.00	0.10	2.27	1.5011	34.3	0.111
TOLUENE	0.54	0.00	0.11	2.38	1.4969	33.91	0.099
ETHYLACETATE	0.55	0.45	0.00	6.02	1.3724	38.09	0.228
DIMETHYLSULFOXIDE	1.00	0.00	0.76	47.2	1.4790	45.11	0.471
ACETONITRILE	0.54	0.19	0.31	38.8	1.3440	45.62	0.460

Pedro et al .(2007), [a] = Burdick and Jackson (2013)

Table 15 shows the solvatochromic parameters for the various solvents used in this study. The regression was implemented using SPSS Statistical Software Version 20.0 at a confidence level of 95 %. For styrene polymerization using BPO as initiator, the regression equation obtained (with coefficient of determination, $R^2 = 0.948$), gave the level of monomer conversion as a function of the solvent parameters as shown in Eq.(83). From the regression expression, it is seen that the π^* parameter (dipolarity / polarizability) has the largest positive effect on the styrene conversion followed by E_TN (normalized E_T), while solvent refractive index showed the largest negative influence on conversion followed by basicity and acidity, in that order. A unit increase

in α , β , E and n will cause reduction on styrene conversion by factor of 1.843, 3.354, 0.018 and 4.365, respectively. On the other hand, a unit increase in π^* and E_T^N will increase conversion by factor of 4.265 and 4.205, respectively. Styrene conversion therefore increases with solvents having high dipolarity / polarizability and E_T^N character but with low refractive index.

$$X = 4.407 + 4.265\pi - 1.843\alpha - 3.354\beta - 0.018E - 4.365n + 4.205E_T^N \quad (83)$$

For the styrene polymerization using BPO blend as initiator, the regression equation obtained (with coefficient of determination, $R^2 = 0.955$), gave the level of monomer conversion as a function of the solvent parameters as shown in Eq. (84). From the regression, it is seen that the E_T^N and π^* parameter (dipolarity / polarizability), in that order, have the largest positive effect on the styrene conversion, while the solvent refractive index show the largest negative effect. Indeed four parameters exact positive influence on conversion while only refractive index shows significant negative effect, in contrast to the observation with BPO initiator. The effect of initiator on the monomer conversion is more apparent from the LSER.

$$X = 1.099 + 0.631\pi + 0.232\alpha + 0.066\beta - 0.016E - 0.834n + 2.032E_T^N \quad (84)$$

The strong positive effect of dipolarity/polarizability established in the present study has been reported for other reactions by previous workers. Horn and Matyjaszewski (2013) reported that π^* show the main positive effect on rate constant of activation in their study of solvent effects in atom transfer radical polymerization using ten different solvents. Similar finding was reported in other studies (Bini *et al.*, 2008; Schleicher and Scurto, 2009). However, the strong negative influence of solvent refractive index is reported in this study for the very first time. The LSER correlation established in this study can be used to predict the conversion achievable from any

solvent, provided the KT parameters of such solvent are known or can be determined experimentally, and thus enable evaluation of its suitability for styrene polymerization.

The result of descriptive statistics carried out on SPSS statistical software version 20.0 environment using coefficient of variation (CV) is summarized in Table 16. The table indicates that n , $E_T(30)$ and π^* are homogeneous ($CV < 0.5$) at 0.05, 0.12 and 0.26, respectively while α , β , E and $E_T(N)$ are not homogeneous ($CV > 0.5$) at 1.22, 1.13, 1.07 and 0.54, respectively. Similarly, the yields (conversion) showed homogeneity at different time with 0.46 (20 minutes), 0.36 (30 minutes through 50 minutes). The Pearson correlation result suggests that at time 20 minutes, there is a significant correlation between conversion and n , $E_T(30)$ at $R = -0.728$ and 0.683 , respectively since $p < 0.05$ significant level. These results imply that increase in n reduces conversion at time 20 minutes while increase in $E_T(30)$ increases conversion at time 20 minutes. At time 30 minutes, there is no significant correlation between conversion and any of the solvent properties. At time 40 minutes, there is a significant correlation between conversion and $E_T(30)$, E_TN at $R = 0.719$ and 0.719 , respectively since $p < 0.05$ significant level. These results imply that increase in $E_T(30)$ and E_TN , respectively increases conversion at time 40 minutes. At time 50 minutes, there is a significant correlation between conversion and $E_T(30)$, E_TN at $R = 0.755$ and 0.752 , respectively since $p < 0.05$ significant level. These results imply that increase in $E_T(30)$ and E_TN , respectively increase conversion when the reaction time is 50 minutes.

The result of descriptive statistics using BPO BLEND as initiator is summarized in Table 17 using coefficient of variation (CV), which indicates that n , $E_T(30)$ and π^* are homogeneous ($CV < 0.5$) at 0.05, 0.12 and 0.26, respectively while α , β , E and E_TN are not homogeneous ($CV > 0.5$) at 1.22, 1.13, 1.07 and 0.54, respectively. Similarly, the conversion showed homogeneity at different reaction time with 0.30 (20 minutes), 0.29 (30 minutes and 40 minutes) and 0.31 (50 minutes). The Pearson correlation result suggests that at time 20 minutes, there is a significant correlation between yield and n at $R = -0.714$, since $p < 0.05$ significant level. This result implies that increase in n reduces conversion at time 20 minutes. At time 30 minutes, there is also a significant correlation between conversion and solvent properties; n , $E_T(30)$ and E_TN at $R = -0.707$, 0.752 and 0.741 , respectively $p < 0.05$ significant level. These results imply that an increase in n caused reduction in conversion, and increase in $E_T(30)$ and E_TN caused increase in conversion when the solvent is allowed to stay at most 30 minutes. At time 40 minutes, there is a significant correlation between conversion and n , $E_T(30)$ at $R = -0.672$ and 0.680 , respectively since $p < 0.05$ significant level. These results show that increase in n caused reduction in conversion while increase in $E_T(30)$ caused an increase in conversion. At time 50 minutes, there is a significant correlation between conversion and, $E_T(30)$ and E_TN at $R = 0.769$ and 0.765 , respectively since $p < 0.05$ significant level. These results show that an increase in, $E_T(30)$ and, E_TN respectively results in an increase in conversion at 50 minutes reaction time.

4.3.3. The overall effect of solvent properties on conversion / Rate of polymerization using BPO as initiator.

The descriptive statistics in Table 18 indicates that the coefficient variation (CV) on conversion, π^* , α , β , E , n , $E_T(30)$ and E_{TN} is obtained as 0.36, 0.25, 1.15, 1.06, 1.01, 0.04, 0.11 and 0.51, respectively. The CV results obtained show that there is homogeneity on conversion, π , n and, $E_T(30)$, since $CV < 0.5$ threshold while α , β , E and E_{TN} are not homogeneous. The Pearson correlation result suggests that there is a significant positive correlation between yield and π^* , α , β , E , n , E_{TN} at $R = 0.393$, 0.462 , 0.356 , 0.441 , 0.690 , 0.683 , respectively since $p < 0.05$ significant level. Further, there is a significant negative correlation between yield and $E_T(30)$ at $R = -0.608$ ($p < 0.05$). These results imply that an increase in the solvent properties; π^* , α , β , E , n , E_{TN} will respectively increase the yield. However, increase in $E_T(30)$ will cause reduction on yield. These results are supported by the multiple correlation obtained as $R = 0.974$ (97.4 %). The variation accounted for in the model is given as $R^2 = 0.948$ (94.8 %); which is the amount of information the independent variables have about the dependent variable. The adequacy of variation in each model is ascertained in the ANOVA Table.

Table 18: Descriptive Statistics and Pearson Correlations

	Yield	π^*	α	β	E	n	$E_T(30)$	E_{TN}	Mean	Std. Deviation	CV	N
Yield	1								0.646	0.235	0.36	28
π^*	0.393*	1							0.644	0.158	0.25	28
α	0.462*	-0.418*	1						0.166	0.191	1.15	28
β	0.356*	0.885*	-0.563*	1					0.251	0.268	1.06	28
E	0.441*	0.683*	-0.281	0.866*	1				17.454	17.636	1.01	28
n	-0.608*	0.226	-0.481*	-0.046	-0.288	1			1.428	0.064	0.04	28
$E_T(30)$	0.690*	0.534*	0.045	0.723*	0.918*	-0.569*	1		39.760	4.492	0.11	28
E_{TN}	0.683*	0.578*	0.020	0.750*	0.932*	-0.528*	0.998*	1	0.283	0.143	0.51	28

*. Correlation is significant at the 0.05 level (1-tailed). $R = 0.974$ (97.4%), $R^2 = 0.948$ (94.8%).

Table 19 : Analysis of Variance (ANOVA)

Model	Sum of Squares	Df	Mean Square	F	Sig.
Regression	1.415	6	0.236	64.375	0.000
Residual	0.077	21	0.004		
Total	1.491	27			

a. Dependent Variable: Yield. b. Predictors: (Constant), E_TN , α , n , π^* , E , β .

The ANOVA in Table 19, shows that the variation in the dependent variable accounted for by the model is adequate at $F = 64.375$, $p < 0.05$. Hence the model is acceptable for result utilization and further analysis. The effect of the independent variables on the dependent variable is examined in the regression analysis contained in Table 20.

Table 20: Regression Analysis Coefficients

Model	Unstandardized Coefficients		Standardized Coefficients	t	Sig.
	B	Std. Error	Beta		
(Constant)	4.407	0.796		5.537	0.000
π^*	4.265	0.664	2.867	6.418	0.000
α	-1.843	0.439	-1.498	-4.200	0.000
β	-3.354	0.673	-3.820	-4.981	0.000
E	-.018	0.004	-1.367	-4.757	0.000
n	-4.365	0.715	-1.192	-6.103	0.000
E_TN	4.205	0.709	2.567	5.933	0.000

Dependent Variable: Conversion.

Multiple regression analysis was used to determine the effect of the independent variables on the dependent variable. Conversion represents the dependent variable, while the solvent properties represent the independent variables. The result of the analysis reveals that all the solvent properties are significant at $t = 6.418, -4.200, -4.981, -4.757, -6.103$ and 5.933 , respectively, $P < 0.05$. Hence, the solvent properties have significant effect on conversion. π^* and E_TN have direct effect on conversion while α , β , E and n have indirect effect on conversion. In addition, $E_T(30)$ was excluded from the model due to redundancy (Table 21).

Table 21: Excluded Variables

Model	Beta In	t	Sig.	Partial Correlation	Collinearity Statistics
					Tolerance
E _T (30)	. ^b	.	.	.	0.000

4.3.4. The overall effect of solvent properties on yield/rate of polymerization using BPO BLEND as initiator.

Table 22: Descriptive Statistics and Pearson Correlations

	Yield	Π^*	α	β	E	n	E _T (30)	E _T N	Mean	Std. Deviation	CV	N
Yield	1								0.668	0.190	0.28	28
Π^*	0.323 [*]	1							0.644	0.158	0.25	28
α	0.542 [*]	-0.418 [*]	1						0.166	0.191	1.15	28
β	0.310	0.885 [*]	-0.563 [*]	1					0.251	0.268	1.06	28
E	0.408 [*]	0.683 [*]	-0.281	0.866 [*]	1				17.454	17.636	1.01	28
n	-0.662 [*]	0.226	-0.481 [*]	-0.046	-0.288	1			1.428	0.064	0.04	28
E _T (30)	0.694 [*]	0.534 [*]	0.045	0.723 [*]	0.918 [*]	-0.569 [*]	1		39.760	4.492	0.11	28
E _T N	0.683 [*]	0.578 [*]	0.020	0.750 [*]	0.932 [*]	-0.528 [*]	0.998 [*]	1	0.283	0.143	0.51	28

*. Correlation is significant at the 0.05 level (1-tailed). R = 0.977 (97.7%). R² = 0.955 (95.5%)

The descriptive statistics in Table 22 indicates that the coefficient of variation (CV) on conversion, π^* , α , β , E, n, E_T(30) and E_TN obtained were 0.28, 0.25, 1.15, 1.06, 1.01, 0.04, 0.11 and 0.51, respectively. The CV results imply that there is homogeneity on yield, π^* , n and E_T(30), since CV < 0.5, threshold while α , β , E and E_TN are not homogeneous. The Pearson correlation result suggests that there is a significant positive correlation between conversion and π^* , α , E, E_T(30), E_TN at R = 0.323, 0.542, 0.408, 0.694, 0.683, respectively since p < 0.05 significant level. Furthermore, there is a significant negative correlation between yield and n at R = -0.662 (p < 0.05). These results imply that increase in the solvent properties; π^* , α , E, E_T(30) and E_TN will respectively increase conversion. However, increase in n will cause reduction on conversion.

These results are supported by the multiple correlation obtained as $R = 0.977$ (97.7%). The variation accounted for in the model is given as $R^2 = 0.955$ (95.5 %); which is the amount of information the independent variables have about the dependent variable. The adequacy of variation in each model is ascertained in the ANOVA table.

Table : 23 Analysis of Variance (ANOVA)

Model	Sum of Squares	df	Mean Square	F	Sig.
Regression	0.933	6	0.156	73.771	0.000
Residual	0.044	21	0.002		
Total	0.977	27			

a. Dependent Variable: Yield

b. Predictors: (Constant), E_{TN} , α , n , π^* , E , β

The ANOVA Table in Table 23 shows that the variation in the dependent variable accounted for by the model is adequate at $F = 73.771$, $p < 0.05$. Hence the model is acceptable for result utilization and further analysis. The effect of the independent variables on the dependent variable is examined in the regression analysis (Table 27).

Table 24: Regression Analysis Coefficients

Model	Unstandardized Coefficients		Standardized Coefficients	t	Sig.
	B	Std. Error	Beta		
(Constant)	1.099	0.604		1.820	0.083
π^*	0.631	0.504	0.524	1.252	0.224
α	0.232	0.333	0.233	0.697	0.494
β	0.066	0.511	0.093	0.130	0.898
E	-0.016	0.003	-1.475	-5.476	0.000
n	-0.834	0.543	-0.281	-1.536	0.139
E_{TN}	2.032	0.538	1.532	3.778	0.001

Dependent Variable: Conversion

Multiple regression analysis was used to determine the effect of the independent variables on the dependent variable. Conversion represents the dependent variable, while the solvent properties

represent the independent variables. The result of the analysis reveals that E and E_{TN} are significant at $t = -5.476$, and $t = 3.778$, $p < 0.05$. Hence, the solvent properties have significant effect on conversion. E_{TN} has direct effect on conversion while E has indirect effect on conversion. Also, $E_T(30)$ was excluded from the model due to redundancy and the rest of the solvent properties are not significant (Table 25).

Table 25: Excluded Variables

Model	Beta In	t	Sig.	Partial Correlation	Collinearity Statistics
					Tolerance
1 $E_T(30)$	. ^b	.	.	.	0.000

a. Dependent Variable: Yield

b. Predictors in the Model: (Constant), E_{TN} , α , n , π^* , E, β

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4.4. Solvent Separation and Selection of Good Solvent

The ease of solvent removal after polymerization is an important consideration in the choice of an appropriate solvent. A suitable method of separating solvent from polystyrene is distillation/evaporation as done in this study, and energy requirement is key. Table 26 lists relevant thermal properties of the seven solvents examined in this study. These properties suffice for a preliminary analysis. The total energy required to vaporize each solvent, as listed in Column 7, is the sum of sensible and latent heat. Acetone and chloroform require the least amount of energy. Toluene, the commonly used solvent, relatively requires higher energy for its separation. An ideal solvent should give high monomer conversion and low energy requirement for its separation. Acetone therefore clearly emerges as the ideal solvent for styrene polymerization on both considerations. Schleicher and Scurto (2009) returned a similar verdict for acetone in their assessment of ten (10) different solvents for the synthesis of ionic liquids, based on three considerations, namely rate of reaction, toxicity and environmental impact

assessment, and total energy for separation. In another recent study, acetone was found to be an excellent solvent for cellulose dissolution due to enhanced polarity in the presence of a well-soluble salt, triethyloctylammonium chloride (Et_3OctNCl) (Kostag *et al.*, 2014).

Table 26: Physical and Thermodynamic Properties of Solvents for Energy Analysis

Solvent	Molecular weight (gmol^{-1})	^a Boiling point T_b ($^{\circ}\text{C}$)	^a $\Delta H_{\text{vap}}(T_b)$ (kJ mol^{-1})	^a C_p at 25°C ($\text{Jg}^{-1}\text{K}^{-1}$)	^b Sensible heat (kJ mol^{-1})	Total heat (kJmol^{-1})
Acetone	58.08	56.1	29.10	2.175	2.06	31.16
Ethylacetate	88.11	77	31.94	1.94	6.32	38.27
Chloroform	119.38	61	29.40	0.69	1.73	31.13
Dimethylsulfoxide	78.13	189	43.10	1.96	22.79	65.89
Acetonitrile	41.05	81.7	29.75	2.23	3.84	33.59
Benzene	78.11	80	33.83	1.74	5.44	39.27
Toluene	92.14	111	38.06	1.71	11.19	49.25

A = Lide (2007) b= Slater and Savelski (2007) , ^bSensible heat = $C_p(T_b - 40^{\circ}\text{C})$

4.5. Polymerization in Acetone / Chloroform Mixture

Sequel to earlier findings in this study, we investigated a possible synergy between acetone which gave the highest conversion and chloroform that has the highest molecular weight was investigated. Figure 17 and Figure 18 show styrene polymerization in co-solvents reaction environment, acetone-chloroform. Styrene conversion and molecular weight of the PS obtained were unexpectedly found to be lower than their respective values in each of the solvents alone. For example, at reaction time of 40 min, 50 % conversion was observed using acetone / chloroform as co-solvents while between about 70 – 80 % conversion was achieved with acetone and chloroform when used separately. There is therefore no synergy between the solvents. This observation makes it unnecessary to have a solvent blend for the polymerization reaction.

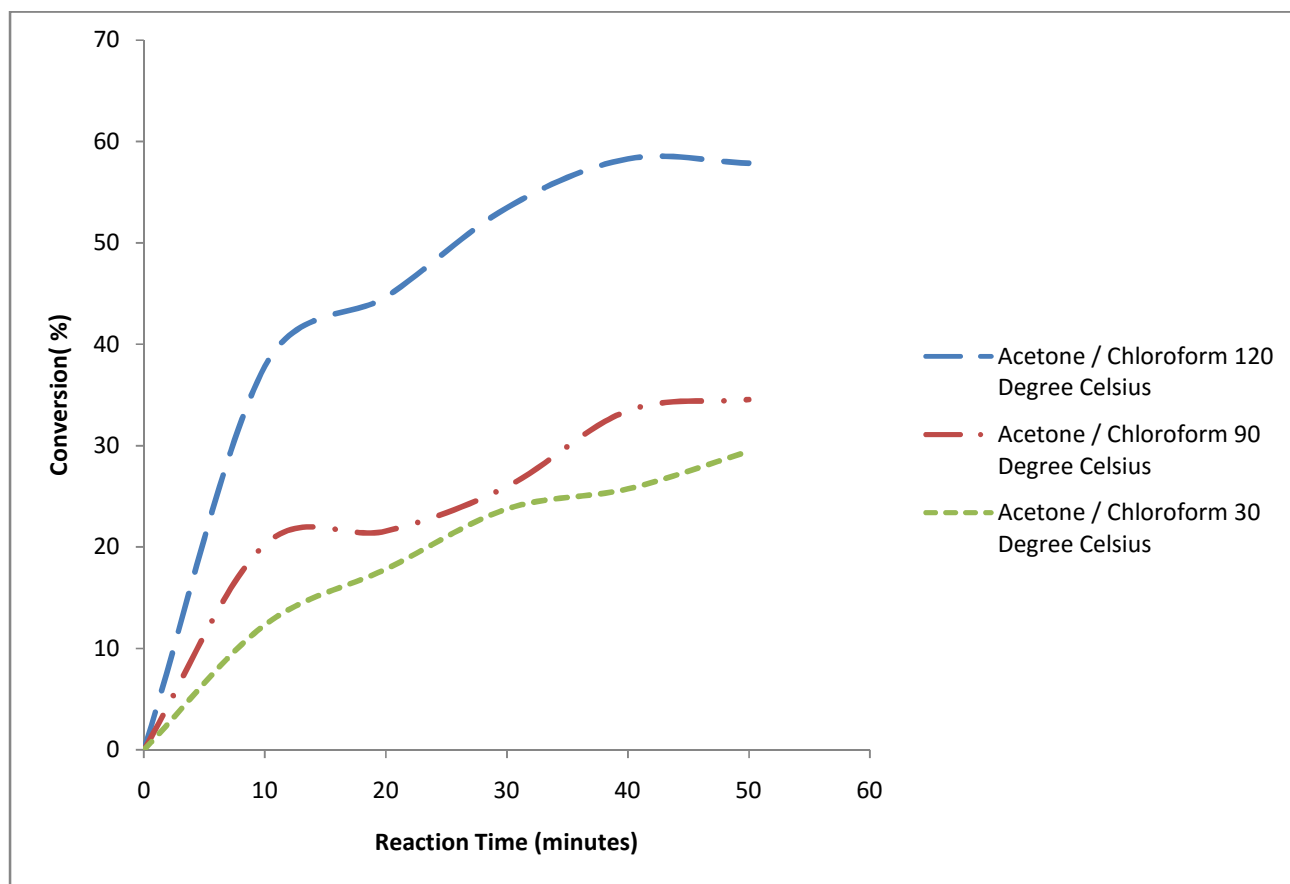


Figure 17: Variation of % conversion with reaction time for acetone /chloroform at different temperature using BPO

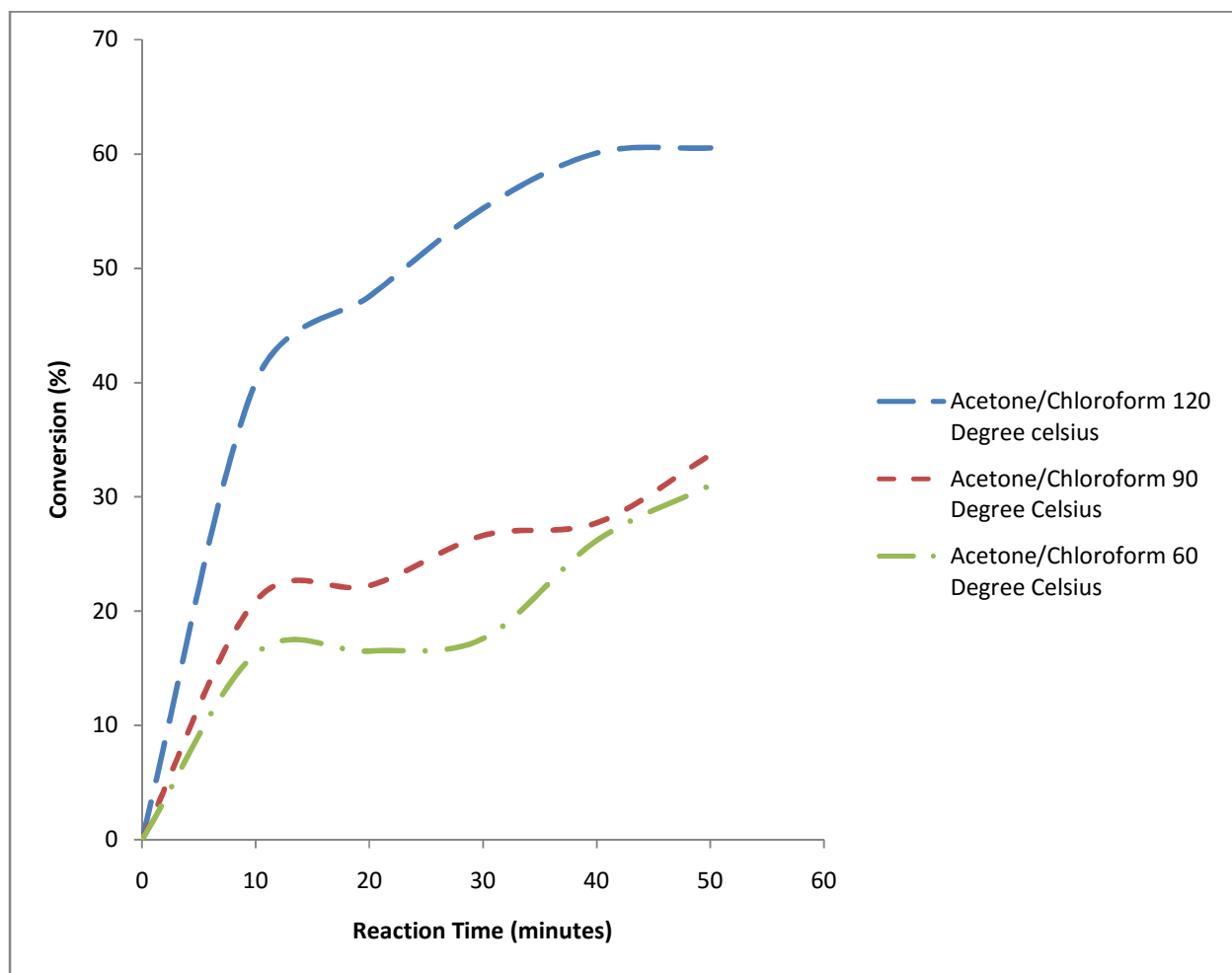


Figure 18: Variation of % conversion with reaction time for acetone / chloroform media at different temperature using BPO Blend

4.6. Polymerization in Green Solvents (Biodiesel and DDW)

The biodiesel obtained from the pawpaw seed oil surprisingly solidified with time indicating the presence or high concentration of phospho-lipids (gum) in the oil. The oil was de-gummed using 2.5 ml of 85 % H_3PO_4 diluted with 30 ml of water. The mixture with the oil was placed in a water-bath for 5 minutes at 60 °C before agitating the mixture in a shaker at 300 rpm for 30 minutes. The resulting mixtures were placed in a centrifuge at high speed for phase separation and characterization as shown in Tables 28 and 29.

Table 27: Physico-chemical properties of the biodiesel.

Test	PSOB	WCOB
Specific Gravity @20 °C	0.867	0.858
API Gravity	31.71	33.42
Viscosity @ 40 °C mm ² /s	1.650	1.890
Heat of combustion kJ/kg	10821.45	10854.06

Table 28: Fatty acid composition of biodiesel

Fatty Acid	PSOB (%) Syed <i>et al.</i> , (2014)	WCOB % (This Study)
Myristic	0.24	4.27
Palmitic	13.5	11.38
*Palmitoleic	0.21	---
Stearic	4.5	10.57
*Oleic	72.5	23.48
*Linoleic	2.90	40.66
*Linolenic	0.23	---
Arachidic	0.39	---
Eicosenoic	0.28	2.56
Lauric	---	2.17
*Paullinic	---	2.59
Behenic	---	2.32

*Unsaturated

Figure 19 and Figure 20 show styrene conversion profile against reaction time for Biodiesel solvents (waste cooking oil biodiesel (WCOB) and pawpaw seed oil biodiesel (PSOB) at different reaction temperature using benzoyl peroxide and its blend with dicyclohexylphthalate as initiators, respectively. WCOB gives a higher conversion compared to PSOB at their corresponding temperature for each of the initiators. At 60 and 90 °C, conversion of styrene in the two green media at about 60 minutes reaction time was found to be approximately the same irrespective of the initiators used. However, appreciable difference was observed at 120 °C with biodiesel obtained from waste cooking oil having a higher conversion of about 34 and 38 % respectively using BPO and BPO BLEND as initiator. From all indications, styrene homopolymerization in biodiesel obtained from waste cooking oil and pawpaw seed oil is being reported for the very first time. Similar reports are either not in existence or unavailable in open literature. The better performance of WCOB is attributed to the chemical pre-treatment it was subjected to. The waste cooking oil at the virgin stage was subjected to harsh and repeated thermodynamic conditions which are likely to have de-natured or fractionated the oil to increase its volatility. The pre-treatment re-natured and further strengthened the potentials of the oil as biodiesel feedstock. Biodiesel solvents gave lower conversion compared to molecular solvents. It is instructive to note that they compared favourably with toluene in the BPO initiator as evident in Fig 13. This is a promising result and it can be inferred that these green solvents can suitably replace toluene in styrene polymerization especially using BPO initiator.

Figure 21 shows styrene polymerization carried out in distilled and de-ionised water at different reaction temperatures using 2-Azobis (2- ethylpropionamidine) dihydrochloride (AIBA) and Potassium persulfate (KPS) initiators. As obtained in the earlier green liquids, conversion was

observed to be a function of temperature. The monomer conversion attained in the two initiators was almost the same at all temperatures and time.

Generally, DDW gave higher conversion compared with WCOB and PSOB although with a different polymerization technique and mechanism i.e. emulsion polymerization for DDW and bio-solution polymerization for WCOB and PSOB.

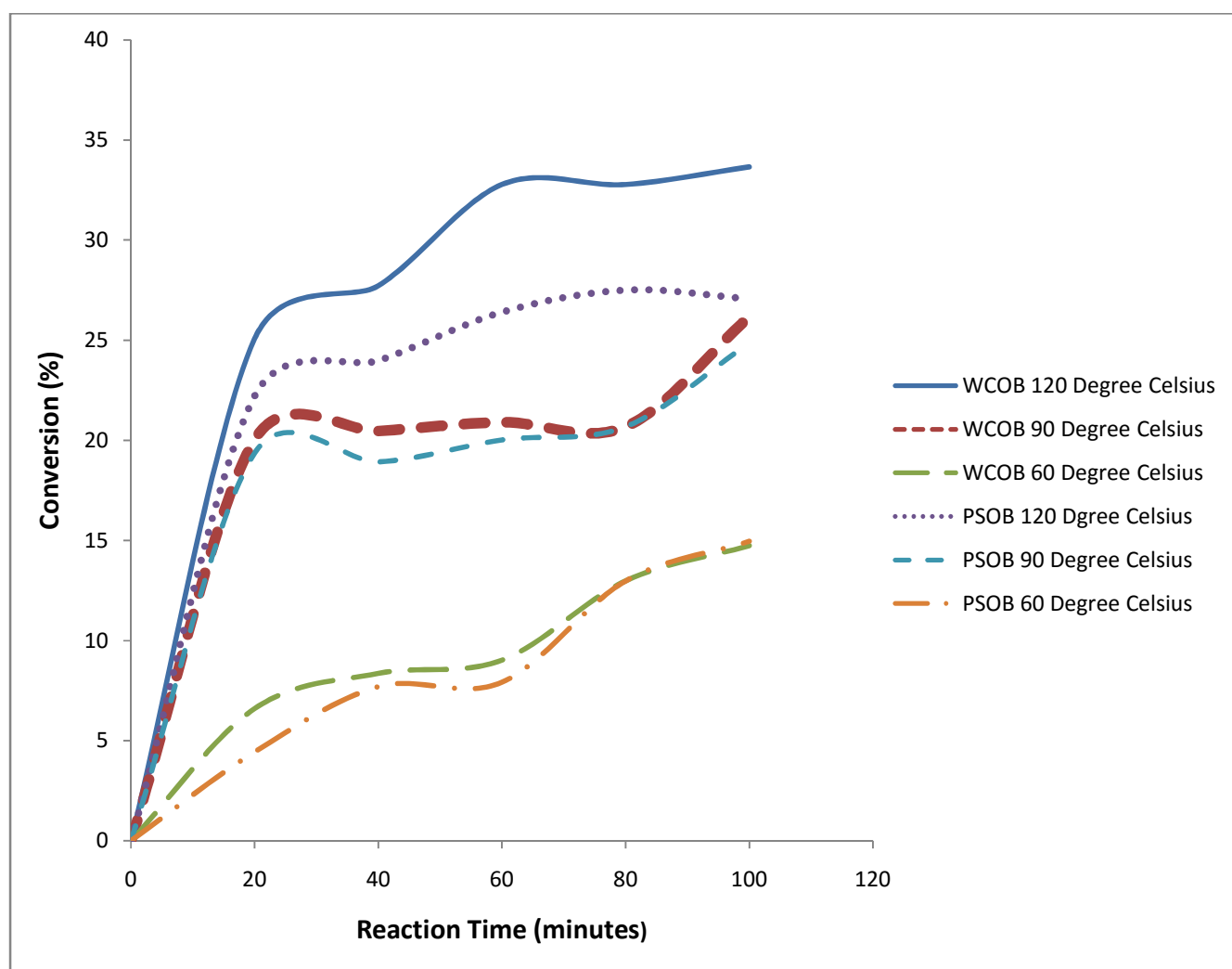


Figure 19 : Variation of Conversion with reaction time for different Green media at different temperature using BPO

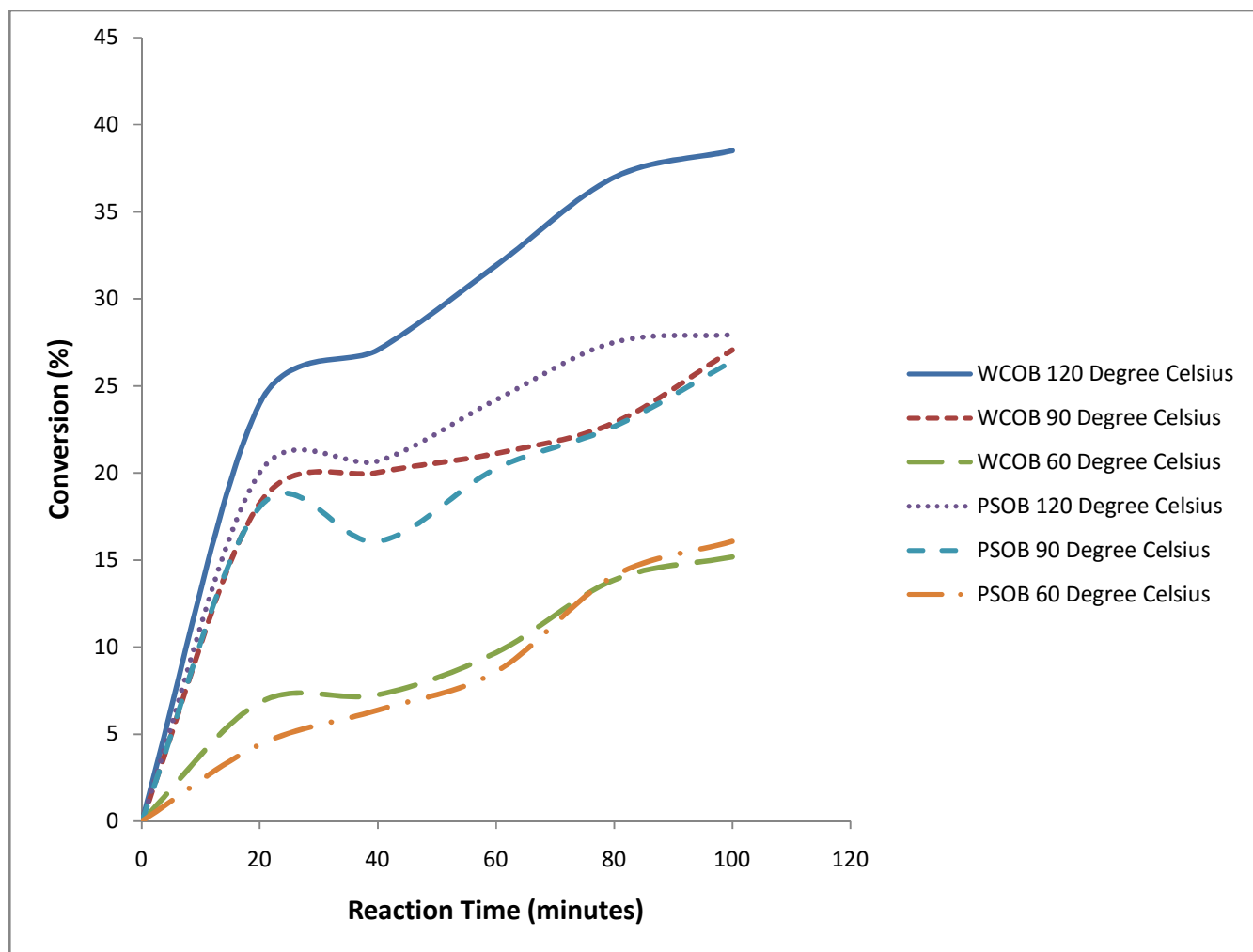


Figure 20: Variation of % conversion with reaction time for different Green media at different temperature using BPO Blend

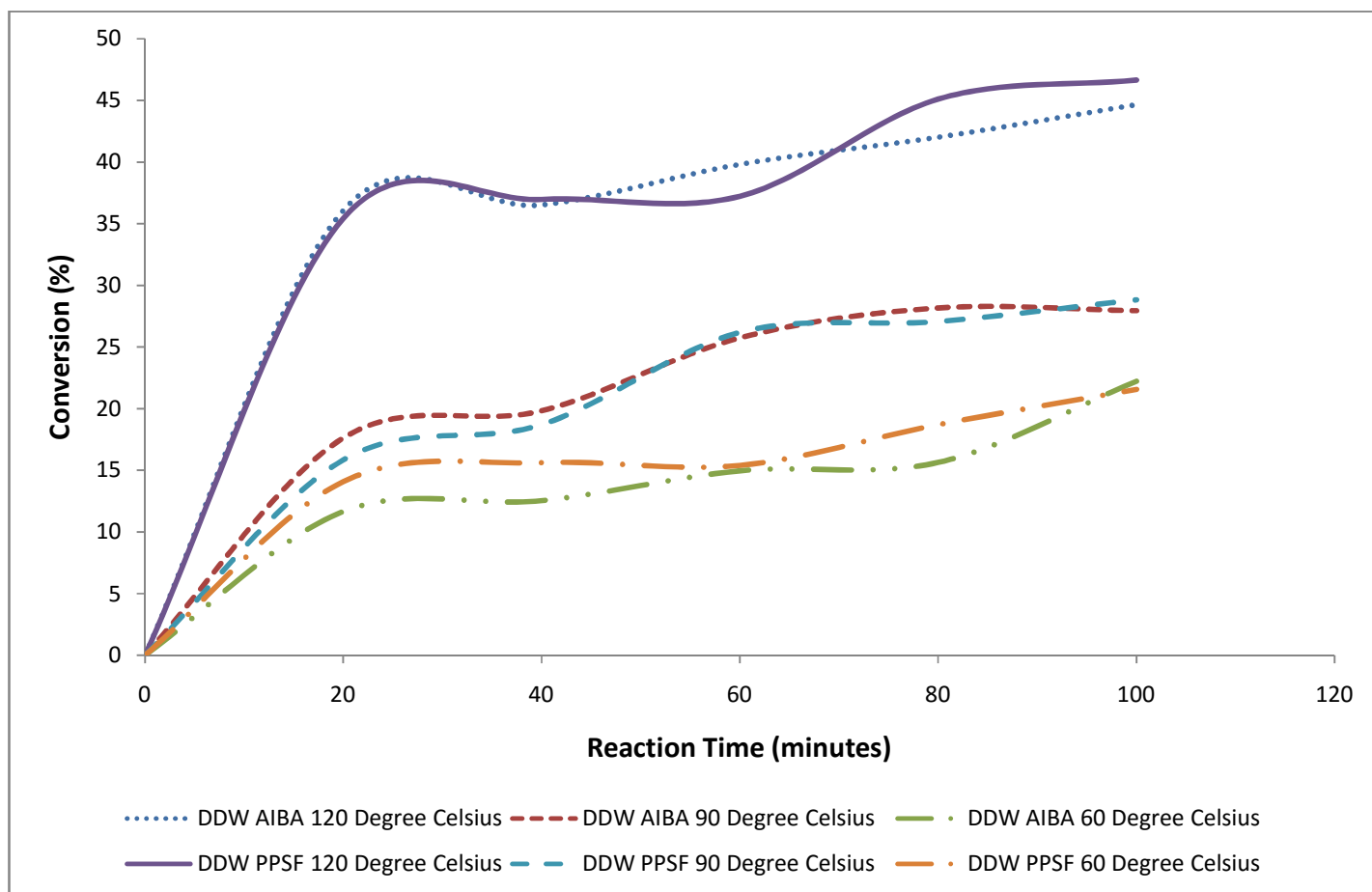


Figure 21: Variation of % conversion with reaction time for DDW using different initiators.

The production of polymers with end use properties is of significant importance to the polymer industry as it directly affects the physical, mechano-chemical, optical and rheological properties of the final product (Verro, 2003). Their processability and end use are directly related to their molecular weight averages. As a result, synthesis of PS of desired molecular weight is very key in polymer industries.

Tables 29 -34 describe the estimation of the solution viscosity molecular weight of the PS. The estimation was carried out using the Mark Houwink Sakurada equation of the form $\eta = 3.7 \times 10^{-4} \times M^{0.62}$ (Goldberg, 2003) at 30 °C where η is the intrinsic viscosity and M is the solution

viscosity molecular weight. Solomon Gatesman and Ciuta, Kuwahara, and Rao and Yaseen equations described in Eq.7 (a-c) were employed against the cumbersome graphical method for the determination of the intrinsic viscosity. Baastiaan, (2005) and other researchers have satisfactorily used these equations, the most used being Solomon and Ciuta (Chrissafis *et al.*, 2005 and Bikiaris *et al.*, 2008). All the samples exhibited molecular weight within acceptable range except for Sample ISC12 synthesized using chloroform as solvent which recorded a value above the acceptable range. Other samples synthesized using same solvent recorded relatively high molecular weight compared to others. However, from the behaviour of the plots shown in Figures 22, there is no serious trend between the type of initiator, solvent used and reaction time to the molecular weight of the PS samples. There is no discernible pattern. This result is in contrary to the observation of Devonport *et al.*, (1997) who had previously shown that number average molecular weights increased in an almost linear fashion with conversion. They revisited the thermal initiation of styrene in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) at 125 °C after conflicting results were reported almost simultaneously by Gaynor *et al.* (1994), Mardare and Matyjaszewski (1994) and Georges *et al.* (1995). Amarjit *et al.*, 2000 also observed that molecular weight of styrene increases with reaction time at ambient temperature for enzyme mediated styrene polymerization. Hui and Hamielec (1972) studied the variations of number-average molecular weight with conversions at four temperatures (100, 140, 170, and 200 °C) and concluded that the molecular weights reduced throughout with the increase in conversion. Shi *et al.*, (1993) also conducted similar study at four different temperatures (140, 160, 180 and 200 °C) and found that the number-average molecular weights did not vary significantly with conversions. Sueo *et al.*, (2003) reported that the molecular weight of polymer formed at lower temperature increases proportionally with the reaction time. In the polymerization at 100 and 140

°C, the molecular weight is independent of reaction time. The above are just few of the numerous inconsistencies in molecular weight data with time or conversion. Reports from researchers globally, which seem conflicting, is due to the complex nature and sensitivity of polymerization reaction even to slight variations in thermodynamic conditions.

Table 29: Molecular weight determination $t_0 = 69$ secs, $[P]$ (g/ml) = 0.13, initiator BPO using Solomon Gatesman and Ciuta Equation

Samples	t(secs)	$\eta_{sp} = \frac{t - t_0}{t_0}$	$\eta_r = \frac{t}{t_0}$	$\eta = \frac{\sqrt{[2(\eta_{sp} - \ln \eta_r)]}}{c}$	$M = \sqrt{\frac{\eta}{K}}$ $\times 10^5$
1SA11	87	0.261	1.261	1.851	9.25988
1SA12	95	0.377	1.377	2.595	15.96324
1SA13	92	0.333	1.333	2.331	13.42340
1SA14	89	0.290	1.290	2.041	10.83979
1SA15	90	0.304	1.304	2.146	11.74900
2SA12	88	0.275	1.275	1.948	10.05999
2SA13	89	0.290	1.290	2.041	10.83979
2SA14	87	0.261	1.261	1.851	9.25988
2SA15	82	0.188	1.188	1.364	5.66169
2SA16	78	0.130	1.130	0.960	3.20863
3SA13	80	0.159	1.159	1.164	4.38402
3SA15	79	0.145	1.145	1.062	3.77582
1SC12	86	0.246	1.246	1.756	8.50959
1SC13	89	0.290	1.290	2.041	10.83979
1SC14	92	0.333	1.333	2.331	13.42340
1SC15	95	0.377	1.377	2.595	15.96324
2SC13	97	0.406	1.406	2.779	17.84361
2SC15	82	0.188	1.188	1.364	5.66169
2SC16	85	0.232	1.232	1.659	7.75466
1SB13	80	0.159	1.159	1.164	4.38402
1SB14	77	0.116	1.116	0.856	2.66814
1SB15	75	0.087	1.087	0.647	1.69794

Table 30: Molecular weight determination $t_0 = 69$ secs, $[P]$ (g/ml) = 0.13, initiator: BPO using Kuwahara Equation

Samples	t(secs)	$\eta_{sp} = \frac{t - t_0}{t_0}$	$\eta_r = \frac{t}{t_0}$	$\eta = \frac{\eta_{sp} + 3\ln\eta_r}{4c}$	$M = \sqrt[3]{\frac{\eta}{K}}$ $\times 10^5$
1SA11	87	0.261	1.261	1.840	9.166636
1SA12	95	0.377	1.377	2.571	15.72161
1SA13	92	0.333	1.333	2.299	13.12701
1SA14	89	0.290	1.290	2.027	10.71511
1SA15	90	0.304	1.304	2.116	11.48590
2SA12	88	0.275	1.275	1.930	9.905794
2SA13	89	0.290	1.290	2.027	10.71511
2SA14	87	0.261	1.261	1.840	9.166636
2SA15	82	0.188	1.188	1.355	5.599699
2SA16	78	0.130	1.130	0.955	3.183974
3SA13	80	0.159	1.159	1.157	4.338463
3SA15	79	0.145	1.145	1.060	3.766873
1SC12	86	0.246	1.246	1.742	8.392955
1SC13	89	0.290	1.290	2.027	10.71511
1SC14	92	0.333	1.333	2.299	13.12701
1SC15	95	0.377	1.377	2.571	15.72161
2SC13	97	0.406	1.406	2.747	17.49394
2SC15	82	0.188	1.188	1.355	5.599699
2SC16	85	0.232	1.232	1.650	7.68881
1SB13	80	0.159	1.159	1.157	4.338463
1SB14	77	0.116	1.116	0.856	2.66958
1SB15	75	0.087	1.087	0.649	1.705572

Table 31: Molecular weight determination $t_0=69$ secs, $[P]$ (g/ml) = 0.13, initiator: BPO using Rao and Yaseen Equation

Samples	t(secs)	$\eta_{sp} = \frac{t - t_0}{t_0}$	$\eta_r = \frac{t}{t_0}$	$\eta = \frac{\eta_{sp} + \ln \eta_r}{2c}$	$M = \sqrt[3]{\frac{\eta}{K}}$ $\times 10^5$
1SA11	87	0.261	1.261	1.896	9.620437
1SA12	95	0.377	1.377	2.680	16.81875
1SA13	92	0.333	1.333	2.386	13.94355
1SA14	89	0.290	1.290	2.095	11.30084
1SA15	90	0.304	1.304	2.190	12.14212
2SA12	88	0.275	1.275	1.992	10.42093
2SA13	89	0.290	1.290	2.095	11.30084
2SA14	87	0.261	1.261	1.896	9.620437
2SA15	82	0.188	1.188	1.386	5.802628
2SA16	78	0.130	1.130	0.970	3.26483
3SA13	80	0.159	1.159	1.179	4.472313
3SA15	79	0.145	1.145	1.078	3.873198
1SC12	86	0.246	1.246	1.792	8.785854
1SC13	89	0.290	1.290	2.095	11.30084
1SC14	92	0.333	1.333	2.386	13.94355
1SC15	95	0.377	1.377	2.680	16.81875
2SC13	97	0.406	1.406	2.872	18.80096
2SC15	82	0.188	1.188	1.386	5.802628
2SC16	85	0.232	1.232	1.695	8.029307
1SB13	80	0.159	1.159	1.179	4.472313
1SB14	77	0.116	1.116	0.868	2.730271
1SB15	75	0.087	1.087	0.655	1.734854

Table 32: Molecular weight determination $t_0 = 69$ secs, $[P]$ (g/ml) = 0.13, initiator: BPO Blend using Solomon Gatesman and Ciuta Equation

Samples	t(secs)	$\eta_{sp} = \frac{t - t_0}{t_0}$	$\eta_r = \frac{t}{t_0}$	$\eta = \frac{\sqrt{[2(\eta_{sp} - \ln \eta_r)]}}{c}$	$M = \sqrt[3]{\frac{\eta}{K}}$ X 10^5
1SA11	87	0.261	1.261	1.851	9.25988
1SA12	89	0.290	1.290	2.041	10.83979
1SA13	88	0.275	1.275	1.948	10.05999
1SA14	87	0.261	1.261	1.851	9.25988
1SA15	88	0.275	1.275	1.948	10.05999
2SA12	77	0.116	1.116	0.856	2.66814
2SA13	82	0.188	1.188	1.364	5.66169
2SA14	83	0.203	1.203	1.463	6.33218
2SA15	79	0.145	1.145	1.062	3.77582
2SA16	77	0.116	1.116	0.856	2.66814
3SA13	76	0.101	1.101	0.752	2.16616
3SA14	88	0.275	1.275	1.948	10.05999
1SC12	103	0.493	1.493	3.300	23.54255
1SC13	93	0.348	1.348	2.413	14.19704
1SC14	89	0.290	1.290	2.041	10.83979
1SC15	91	0.319	1.319	2.229	12.48749
2SC13	92	0.333	1.333	2.331	13.42340
2SC15	90	0.304	1.304	2.146	11.74900
2SC16	91	0.319	1.319	2.229	12.48749

Table 33: Molecular weight determination $t_o = 69$ secs, $[P] \text{ (g/ml)} = 0.13$, initiator: BPO

Blend using Kuwahara Equation.

Samples	t(secs)	$\eta_{sp} = \frac{t - t_o}{t_o}$	$\eta_r = \frac{t}{t_o}$	$\eta = \frac{\eta_{sp} + \ln \eta_r}{2c}$	$M = \sqrt[3]{\frac{\eta}{K}}$ X 10^5
1SA11	87	0.261	1.261	1.8450	9.166636
1SA12	89	0.290	1.290	2.027	10.71511
1SA13	88	0.275	1.275	1.930	9.90579.4
1SA14	87	0.261	1.261	1.830	9.166636
1SA15	88	0.275	1.275	1.930	9.905794
2SA12	77	0.116	1.116	0.856	2.66958
2SA13	82	0.188	1.188	1.355	5.599699
2SA14	83	0.203	1.203	1.457	6.289565
2SA15	79	0.145	1.145	1.060	3.766873
2SA16	77	0.116	1.116	0.856	2.66958
3SA13	76	0.101	1.101	0.749	2.152864
3SA14	88	0.275	1.275	1.930	9.905794
1SC12	103	0.493	1.493	3.260	23.06658
1SC13	93	0.348	1.348	2.392	13.99800
1SC14	89	0.290	1.290	2.027	10.71511
1SC15	91	0.319	1.319	2.211	12.32749
2SC13	92	0.333	1.333	2.299	13.12701
2SC15	90	0.304	1.304	2.116	11.48590
2SC16	91	0.319	1.319	2.211	12.32749

Table 34: Molecular weight determination $t_0 = 69$ secs, $[P]$ (g/ml) = 0.13, initiator: BPO Blend using Rao and Yaseen Equation.

Samples	t(secs)	$\eta_{sp} = \frac{t - t_0}{t_0}$	$\eta_r = \frac{t}{t_0}$	$\eta = \frac{\eta_{sp} + \ln \eta_r}{2c}$	$M = \sqrt[3]{\frac{\eta}{K}}$ X 10^5
1SA11	87	0.261	1.261	1.896	9.620437
1SA12	89	0.290	1.290	2.095	11.30084
1SA13	88	0.275	1.275	1.992	10.42093
1SA14	87	0.261	1.261	1.896	9.620437
1SA15	88	0.275	1.275	1.992	10.42093
2SA12	77	0.116	1.116	0.868	2.730271
2SA13	82	0.188	1.188	1.387	5.802628
2SA14	83	0.203	1.203	1.492	6.534852
2SA15	79	0.145	1.145	1.078	3.873198
2SA16	77	0.116	1.116	0.868	2.730271
3SA13	76	0.101	1.101	0.759	2.195631
3SA14	88	0.275	1.275	1.992	10.42093
1SC12	103	0.493	1.493	3.438	25.12365
1SC13	93	0.348	1.348	2.487	14.90511
1SC14	89	0.290	1.290	2.095	11.30084
1SC15	91	0.319	1.319	2.292	13.06422
2SC13	92	0.333	1.333	2.386	13.94355
2SC15	90	0.304	1.304	2.190	12.14212
2SC16	91	0.319	1.319	2.292	13.06422

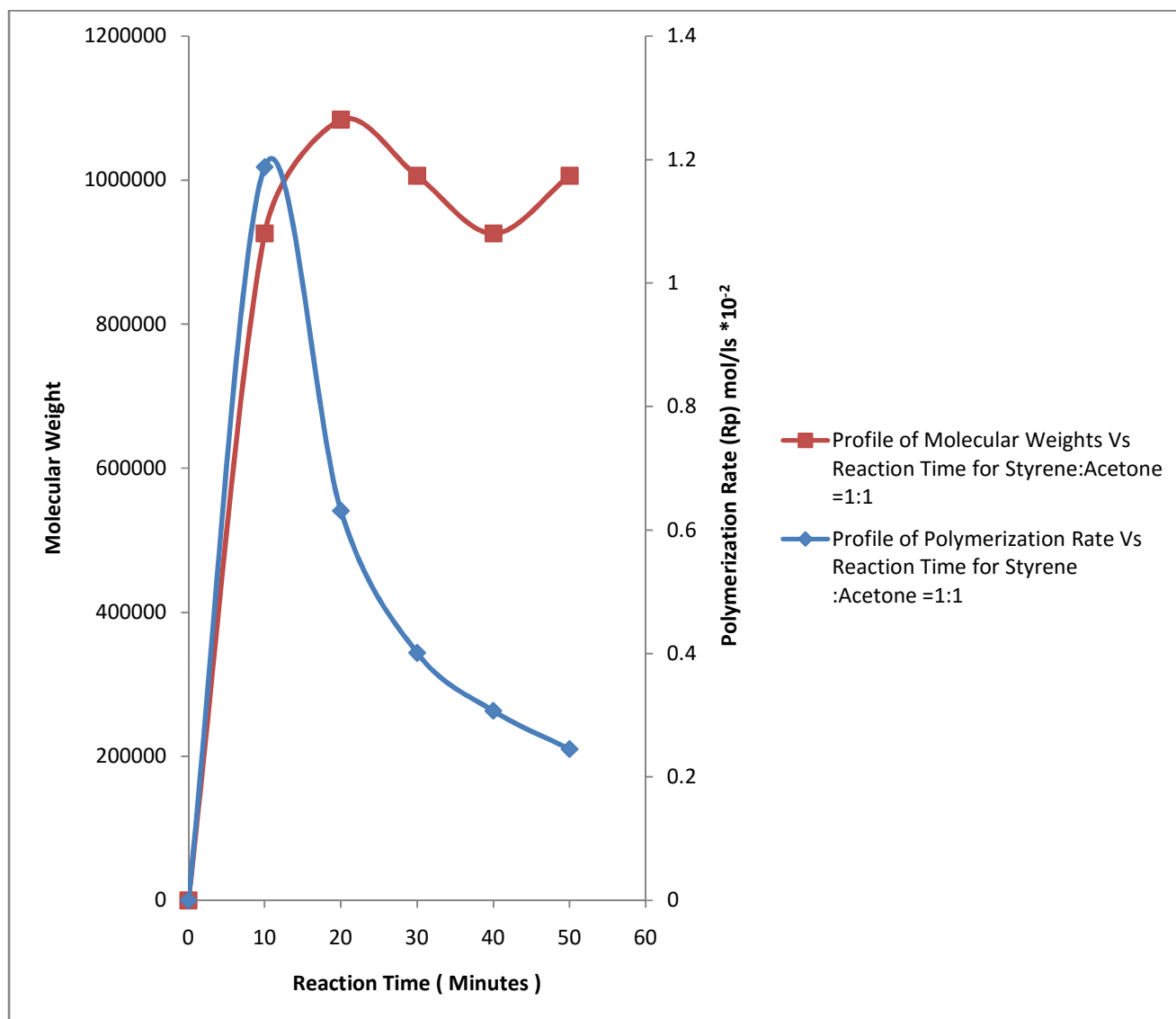


Figure 22 : Variation of molecular weight / polymerization rate (Rp) with reaction time

Aside the molecular weights, the synthesized PS were further subjected to both solubility and density test as shown in Table 44. As expected, the samples were readily soluble in non-polar solvents and the density was between the expected ranges.

4.7. Comparison of Experimental data with modeled results

Equation (55) earlier derived represents our model which was able to predict lower styrene conversion especially when poor polar solvents such as toluene is used but fail completely to predict high styrene conversion. The model was improved upon and modified by the introduction of the Trommsdorf Norrish (gel) effect (Eq.58) to obtain modified model (Eq.64). The modified model which is a polynomial of order four was solved using Maple 17.1 environment. Complex and negative roots obtained for the conversion were rejected.

Figure 23 compares the results of both the kinetic model and the statistical model. They both compare well with the experimental data. The Figure also depicts the degree of improvement on the earlier styrene conversion model. The improved model was found to mimic the experimental data up to the 30 minutes reaction time after which a very slight deviation was observed. Our previous conversion model exhibited same behaviour with that of Garg *et al.*, (2014). The exclusion of the gel effect in the their conversion model may likely be responsible for its poor predicting potentials.

Equations 12-17 as earlier stated were solved analytically as carried out by Garg *et al.*, (2014) for the calculation of the live moments of radicals and dead moments of polymers (Eqs. 67-74) and the subsequent average properties (M_n , M_w , PDI) of the polymer. We however present herein a summary of the analytical solution.

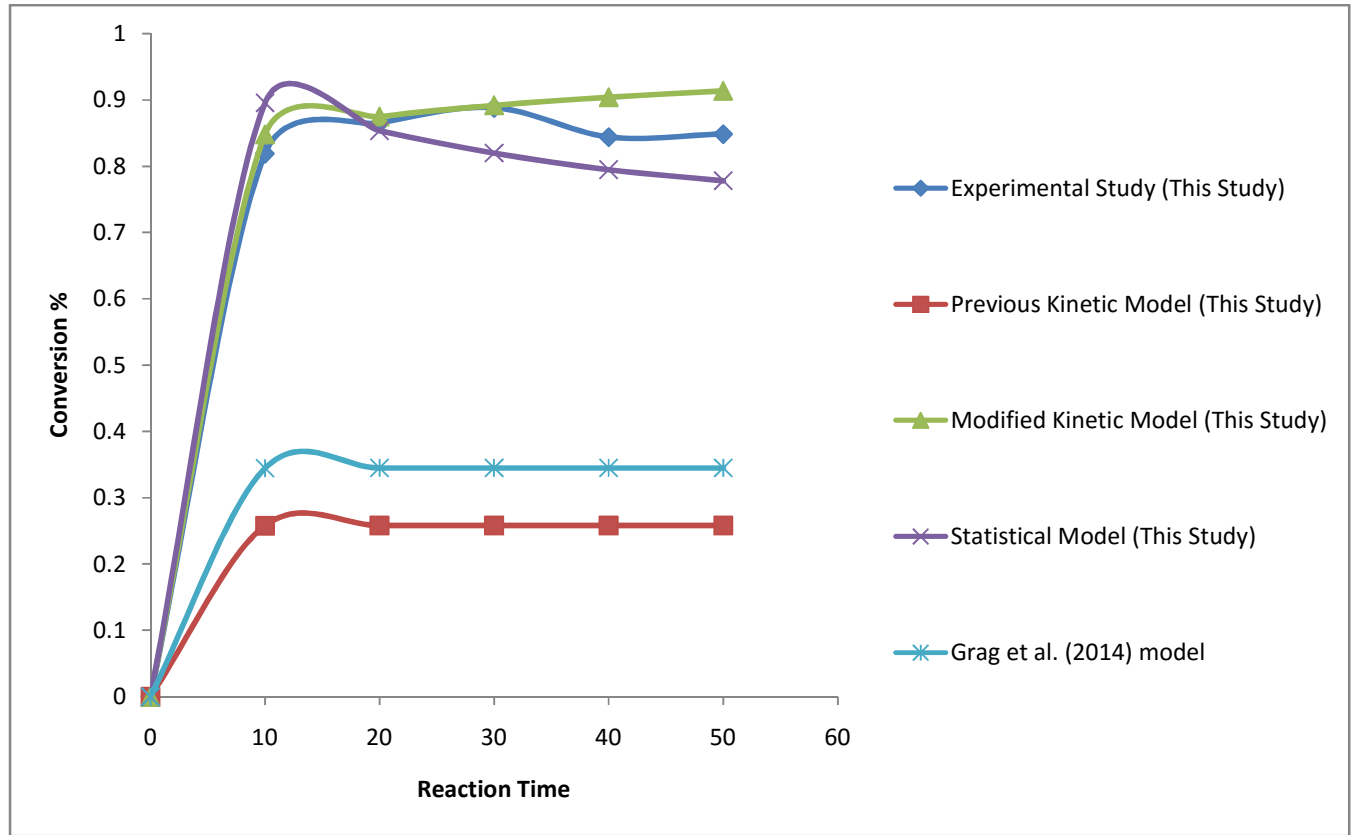


Figure 23: Comparison of Experimental data with modeled results

4.7.1 : Analytical solution of the system of Equations. 67-74.

$$\lambda_0 = \sqrt{\frac{2fk_d I_0}{k_t}} \quad (85)$$

$$\lambda_1 = \lambda_0 \left[\frac{1+L}{1+R_p L} \right] \quad (86)$$

$$\lambda_2 = \lambda_0 \left\{ \frac{1+(3-R_p)L+(2-R_p)L^2}{(1+R_p L)^2} \right\} \quad (87)$$

$$\mu_0 = R_M \{M_0 \quad M\} + \{S_0 \quad S\} + \left(1 - \frac{R_T}{2}\right) \cdot 2f \cdot \{I_0 \quad I\} \quad (88)$$

$$\mu_1 = \{M_0 \quad M\} + \{S_0 \quad S\} + 2f \{I_0 \quad I\} \quad (89)$$

When $R_L < 0.1$, $P \approx 2 + R_T$

$$\mu_2 = P \cdot (1 + R_{SM})^2 \cdot D_0 \cdot \left[\sum_{m=1}^{\infty} \left(\frac{C_0^m}{m.m!} - \frac{(C_0 y)^m}{m.m!} \right) \ln y \right] + (2p - 1) \cdot (1 + R_{SM}) \cdot \{M_0 - M\} + (P - 1) \cdot 2f \cdot \{I_0 - I\} \quad (90)$$

$$\text{When } 10 > R_L \geq 0.1, P = \frac{2}{R_L + 1} + \frac{R_T}{(R_L + 1)^2}$$

$$\mu_2 = P \cdot (1 + R_{SM})^2 \cdot D_0 \cdot \left[\sum_{m=1}^{\infty} \left(\frac{C_0^m}{m.m!} - \frac{(C_0 y)^m}{m.m!} \right) \ln y \right] + (2p - 1) \cdot (1 + R_{SM}) \cdot \{M_0 - M\} + (P - 1) \cdot 2f \cdot \{I_0 - I\} \quad (91)$$

When $R_L \geq 10$,

$$L = \frac{k_{pr} M \lambda_0}{2f k_d I} \quad (92a)$$

$$\mu_2 = \left(\frac{2}{R_p} (1 + R_{SM})^2 - (1 + R_{SM}) \cdot \{M_0 - M\} + \left(\frac{R_T}{R_p^2} (1 + R_{SM})^2 + \frac{4}{R_p} (1 + R_{SM}) \right) \right) \cdot 2f \cdot \{I_0 - I\} \quad (92b)$$

$$R_p L = \frac{k_{fm} M + k_{fs} S}{k_t \lambda_0} = R_L \quad (92c)$$

$$R_p = \frac{k_{fm}}{k_{pr}} + R_{SM} \quad (92d)$$

$$R_T = \frac{k_{tc}}{k_t} \quad (92e)$$

$$D_0 = \frac{2(k_{pr} M_0)^2}{k_t \lambda_0} e^{-C_0} \quad (92f)$$

$$C_0 = 2B_0 \quad (92g)$$

$$y = e^{\frac{-k_d t}{2}} \quad (92h)$$

The PDI sometimes called heterogeneity ratio, dispersion ratio or non-uniformity coefficient is commonly used for the description of the polymer molecular weight distribution (MWD). Similarly, the values of the live moments are infinitesimally small compared to their corresponding dead moments (Table 36). The reports of many researchers such as Christophe *et al.*, (2005), Kiparissides *et al.*, (2003), Hui and Hamielec (1972) and Gao and Penlidis (1998) further confirmed the extremely low value of the live moments by modifying Eq.(11c) as $PDI =$

$\frac{M_w}{M_n} \approx \frac{\mu_2 \mu_0}{\mu_1^2}$. The PDI is a measure of the heterogeneity of sizes of molecules in the synthesized

PS. Polymers of nature are typically monodispersed with PDI value of 1.00 (Brown, 2012). This value indicates perfect uniformity, in which all molecules about (6.02×10^{23}) have exactly the same molecular weight. Rogosic *et al.*, (1996) in their research concluded that higher PDI indeed implies wider MWD. However, contrary to the widely accepted belief, the reverse is not true. Similarly, as against the widely believed physical significance of PDI, Mencer (1988) debunked that the ratio is an absolute measure of the molecular weight distribution of polymers. In the light of these, the main molecular weight of polymers remains a key parameter to characterize polymers especially in terms of physical property-processability relationship. Pinto *et al.*, (2001) further stated that temperature variation may affect negatively the quality of the polymer produced since changes in the polymerization temperature cause increase in PDI.

Table 35: PS average properties at different reaction conditions

Samples/ Time(min)	Live moments			Dead moments			Average properties		
	$\lambda_0 \times 10^9$	$\lambda_1 \times 10^9$	$\lambda_2 \times 10^9$	μ_0	μ_1	μ_2	M_w	M_n	PDI
1a/10	9.9	0.204	0.632	0.04828	0.07394	0.23510	330.65	159.30	2.076
1b/10	8.6	0.191	0.653	0.03628	0.05854	0.21306	378.54	167.80	2.256
1c/10	7.0	0.175	0.695	0.02417	0.04234	0.18892	464.08	182.18	2.547
1d/10	5.0	0.154	0.805	0.01205	0.02489	0.16111	673.17	214.74	3.135
2a/10	2.3	4.6	0.139	0.00299	0.00596	0.03481	607.46	207.18	2.932
2b/10	2.0	4.3	0.143	0.00225	0.00482	0.03297	711.14	223.03	3.189
2c/10	1.6	3.9	0.152	0.00150	0.00360	0.03091	893.26	249.84	3.575
2d/10	1.1	3.4	0.174	0.00075	0.00223	0.02844	1325.99	310.50	4.270
3a/20	9.9	0.351	0.021	0.06830	0.11046	0.41430	390.04	168.19	2.319
3b/20	8.6	0.376	0.023	0.05133	0.08789	0.38092	450.72	178.07	2.531
3c/20	7.0	0.321	0.026	0.03419	0.06404	0.34414	558.83	194.79	2.869
3d/20	4.96	0.302	0.034	0.01706	0.03815	0.30137	821.56	232.61	3.532
4a/20	2.26	4.65	1.45	0.00588	0.01176	0.06935	613.46	208.11	2.948
4b/20	1.95	4.35	0.149	0.00442	0.00951	0.06572	718.31	224.10	3.205
4c/20	1.60	3.99	0.159	0.00294	0.00710	0.06164	902.44	251.15	3.59
4d/20	1.13	3.52	0.184	0.00147	0.00441	0.05677	1339.76	312.37	4.289
5a/30	9.9	0.704	0.093	0.07661	0.12938	0.56400	453.36	175.63	2.581
5b/30	8.6	6.92	0.00104	0.05758	0.10334	0.52458	527.94	186.66	2.828

5c/30	7.0	0.676	0.00123	0.03835	0.07572	0.48093	660.54	205.32	3.217
5d/30	5.0	0.656	0.00167	0.01913	0.04554	0.42982	981.62	247.55	3.965
6a/30	2.3	4.7	0.151	0.00866	0.01740	0.10362	619.49	209.03	2.964
6b/30	2.0	4.4	0.157	0.00650	0.01408	0.09824	725.52	225.17	3.222
6c/30	1.6	4.1	0.167	0.00433	0.01052	0.09220	911.67	252.47	3.611
6d/30	1.1	3.6	0.195	0.00216	0.00653	0.08499	1353.60	314.24	4.308
7a/40	9.9	0.157	0.00472	0.08006	0.13965	0.69748	519.41	181.41	2.863
7b/40	8.6	0.016	0.00538	0.06017	0.11184	0.65470	608.76	193.33	3.149
7c/40	7.0	0.153	0.00651	0.04008	0.08228	0.60722	767.47	213.51	3.595
7d/40	5.0	0.015	0.00906	0.01999	0.04982	0.55136	1150.96	259.17	4.44
8a/40	2.3	4.8	0.158	0.01133	0.02288	0.13762	625.56	209.96	2.979
8b/40	2.0	4.5	0.164	0.00851	0.01852	0.13054	732.77	226.24	3.239
8c/40	1.6	4.2	0.176	0.00567	0.01384	0.12259	920.95	253.79	3.629
8d/40	1.1	3.7	0.206	0.00283	0.00860	0.11310	1367.52	316.11	4.326
9a/50	9.9	0.0361	0.00026	0.08149	0.14547	0.82157	587.36	185.65	3.164
9b/50	8.6	0.0360	0.00029	0.06124	0.11674	0.77700	692.20	198.24	3.492
9c/50	7.0	0.3588	0.00036	0.04080	0.08611	0.72730	878.39	219.53	4.001
9d/50	5.0	0.0357	0.00051	0.02035	0.05238	0.66871	1327.80	267.70	4.960
10a/50	2.3	4.9	0.166	0.01391	0.02821	0.17136	631.67	210.89	2.995
10b/50	2.0	4.6	0.172	0.01046	0.02285	0.16263	740.07	227.31	3.256
10c/50	1.6	4.3	0.185	0.00697	0.01709	0.15283	930.29	255.10	3.647
10d/50	1.1	3.8	0.218	0.00347	0.01062	0.14111	1381.52	317.98	4.345

There are many parameters that control molecular weight of the synthesized PS. Tables 40 and 41 show a clearer trend of how some of these parameters such as reaction time, temperature and initiator concentration affects polymer average properties such as M_w , M_n and the estimated PDI.

Table 36: Changes in PS average properties and PDI with reaction parameters (BPO)

Reaction time (min)	M_w	M_n	Polydispersity
<i>363 K, $I_0=0.0825$ mol/L</i>			
10	330.65	159.30	2.076
20	390.04	168.19	2.319
30	453.36	175.63	2.581
40	519.41	181.41	2.863
50	587.36	185.65	3.164
<i>363 K, $I_0=0.0620$ mol/L</i>			
10	378.54	167.80	2.256
20	450.72	178.07	2.531
30	527.94	186.66	2.828
40	608.76	193.33	3.149
50	692.20	198.24	3.492
<i>363 K, $I_0=0.0413$ mol/L</i>			
10	464.08	182.18	2.547
20	558.83	194.79	2.869
30	660.54	205.32	3.217
40	767.47	213.51	3.595
50	878.39	219.53	4.001
<i>363 K, $I_0=0.0206$ mol/L</i>			
10			
20	673.17	214.74	3.135
30	821.56	232.61	3.532
40	981.62	247.55	3.965
50	1150.96	259.17	4.440
	1327.80	267.70	4.960

Table 37: Changes in PS average properties and PDI with Reaction Parameters.(BPO BLEND)

Reaction time (min)	M_w	M_n	Polydispersity
333 K, $I_0=0.0825$ mol/L			
10	607.46	207.18	2.932
20	613.46	208.11	2.948
30	619.49	209.03	2.964
40	625.56	209.96	2.979
50	631.67	210.89	2.995
333 K, $I_0=0.0620$ mol/L			
10	711.14	223.03	3.189
20	718.31	224.10	3.205
30	725.52	225.17	3.222
40	732.77	226.24	3.239
50	740.07	227.31	3.256
333 K, $I_0=0.0413$ mol/L			
10	893.26	249.84	3.575
20	902.44	251.15	3.590
30	911.67	252.47	3.611
40	920.95	253.79	3.629
50	930.29	255.10	3.647
333 K, $I_0=0.0206$ mol/L			
10			
20	1325.99	310.50	4.270
30	1339.76	312.37	4.289
40	1353.60	314.24	4.308
50	1367.52	316.11	4.326
	1381.52	317.98	4.345

Average polymer properties contained in Tables 36 and 37 when compared with other various reports such as that of Wen–Yan *et al.*, (2010), Noro *et al.*, (2005) and Lynd *et al.*, (2007) can conclude that the choice of polymerization agents, nature of solvent, initiator and polymerization temperature, as well as the ratio of dose of reagents introduced during reaction have an impact on the final PS and its corresponding PDI. It was noticed that there was a

reduced value of M_n and M_w at high temperature. Teferal *et al.*, (1997) similarly reported same trend but failed to adduce reason for such inspite of the detailed work done.

The weight average and number average molecular weight history with time are presented in Figures 24 and 25 at different reaction temperature. The respective polydispersity histories are simultaeneously shown on the two figures. With increase in reaction time, a noticeable increase in M_w and M_n is observed accompanied by small increase in PDI. Similar trend was observed by Kissin *et al.*, (1999) and Hakim *et al.*, (2008).

A high value for PDI of about 17.5 was recently reported by Yanyan *et al.*, (2014) in his study of optimization on molecular size distribution in synthesis of polyoxymethylene dimethylethers and using RSM. Tables 37 and 38 shows that all the average properties, including PDI, increase at different rates with reaction time. The implication is that, the longer the polymerization time, especially at high conversion, the probability of termination reactions will increase. With increasing termination, PDI will also increase. Wen-Yan *et al.*, (2010) reported that increase in molecular weight and polydispersity occurs when monomer conversion is higher than 70 %, indicating that the branching taking place between the branched chains is significant and highly branched chains are mainly formed at this stage.

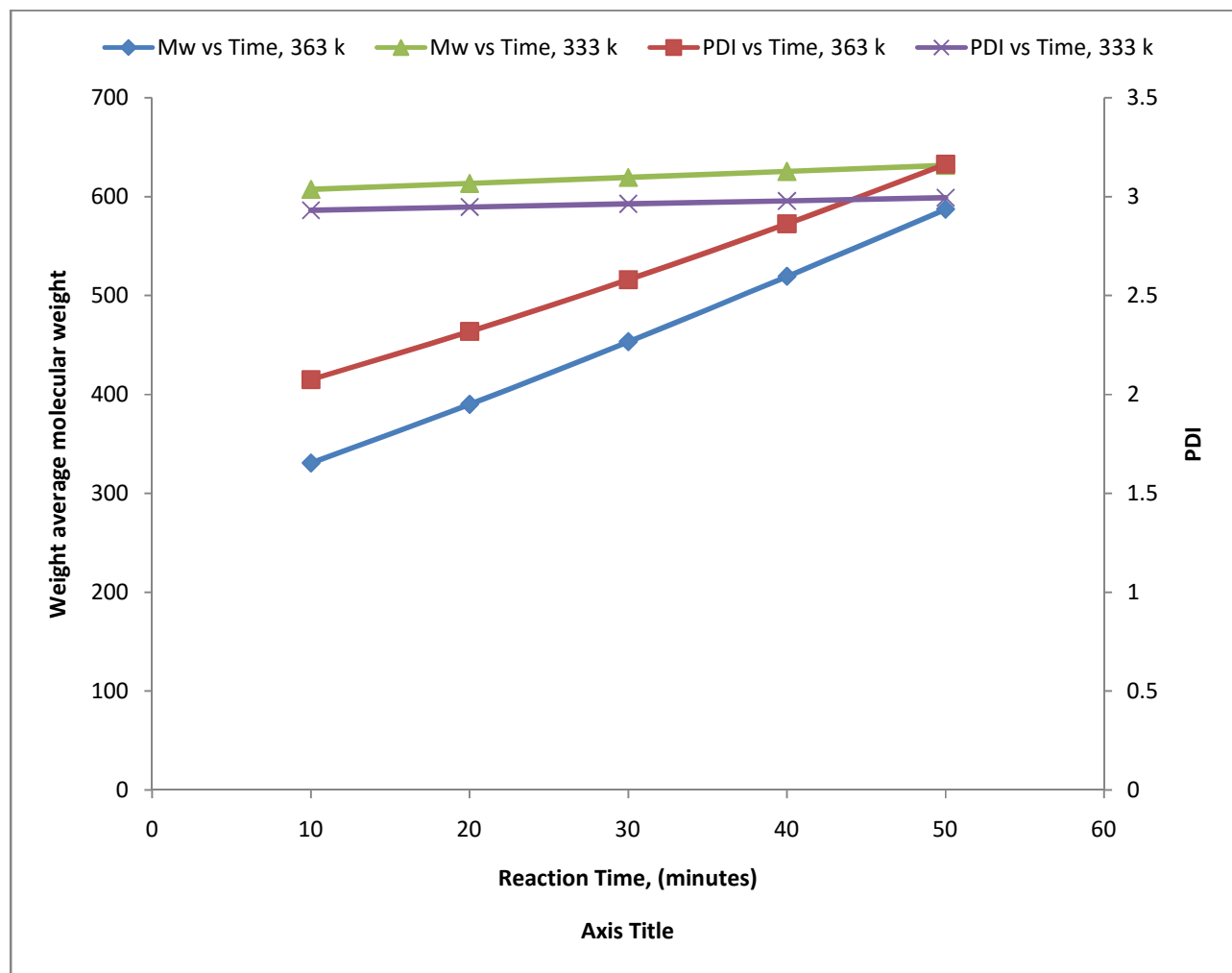


Figure 24: Plot of M_w and PDI vs time at constant initiator concentration (BPO)

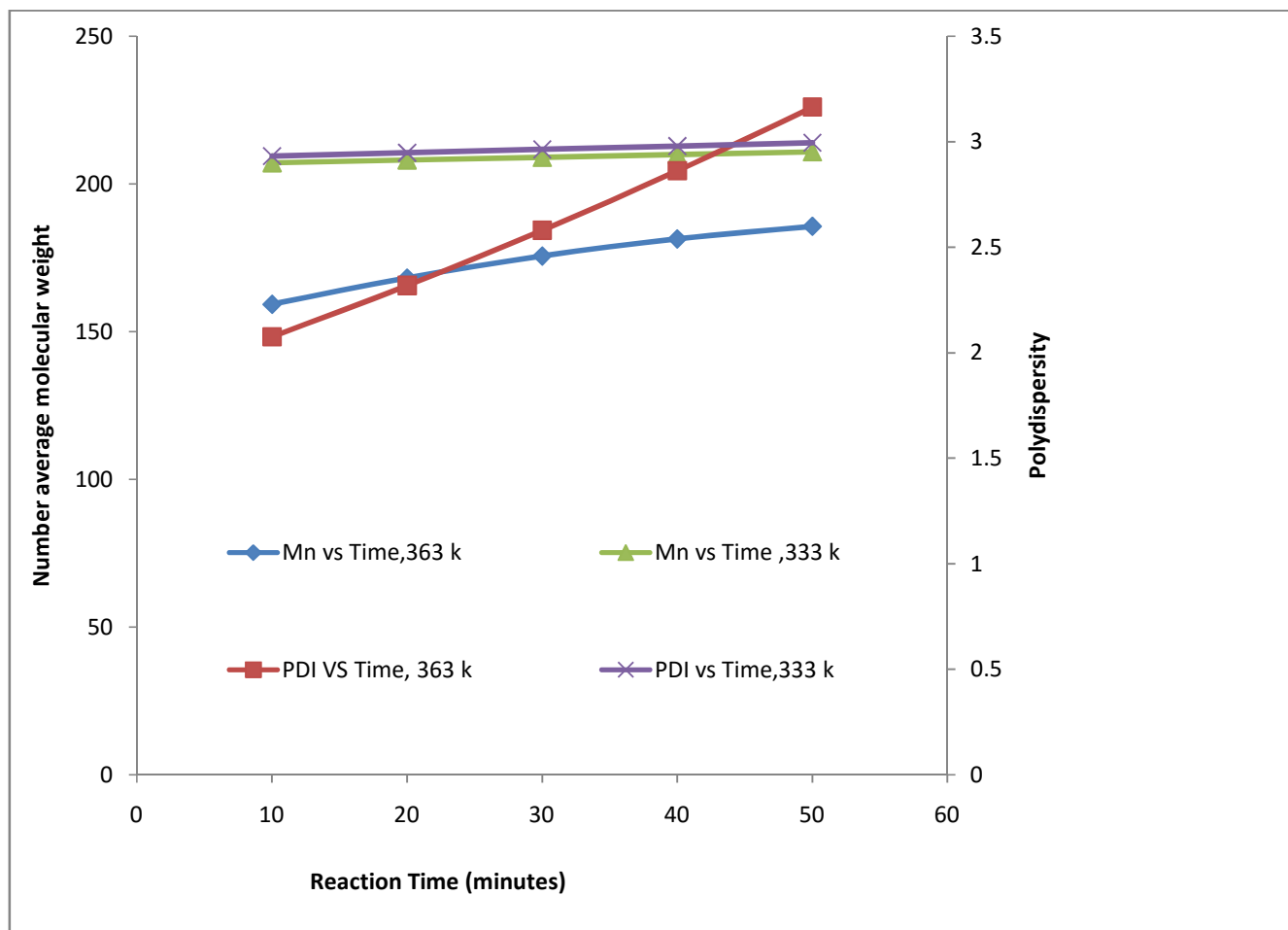


Figure 25: Plot of M_n and PDI vs time at constant initiator concentration (BPO BLEND)

In all for a maximum reaction time, the PDI values were in the range between 2.076 – 4.345 at temperature regimes considered. Both M_n and M_w as depicted by Figures 24-25 increase with reaction time presumably due to the free radical process, Amarjit *et al.*, (2000). The figures depict that PDI increases slightly with time with a more linear increase at higher temperature. This trend was similarly observed in the data published by Ivanchev *et al.*, (2004).

Both M_w and M_n are on same axis of Figure 26. A sharp increase in M_w with PDI is observed compared with M_n . The M_w line is above that of M_n showing that $M_w > M_n$. This trend is a common expectation in the studies of polymer molecular weight distribution.

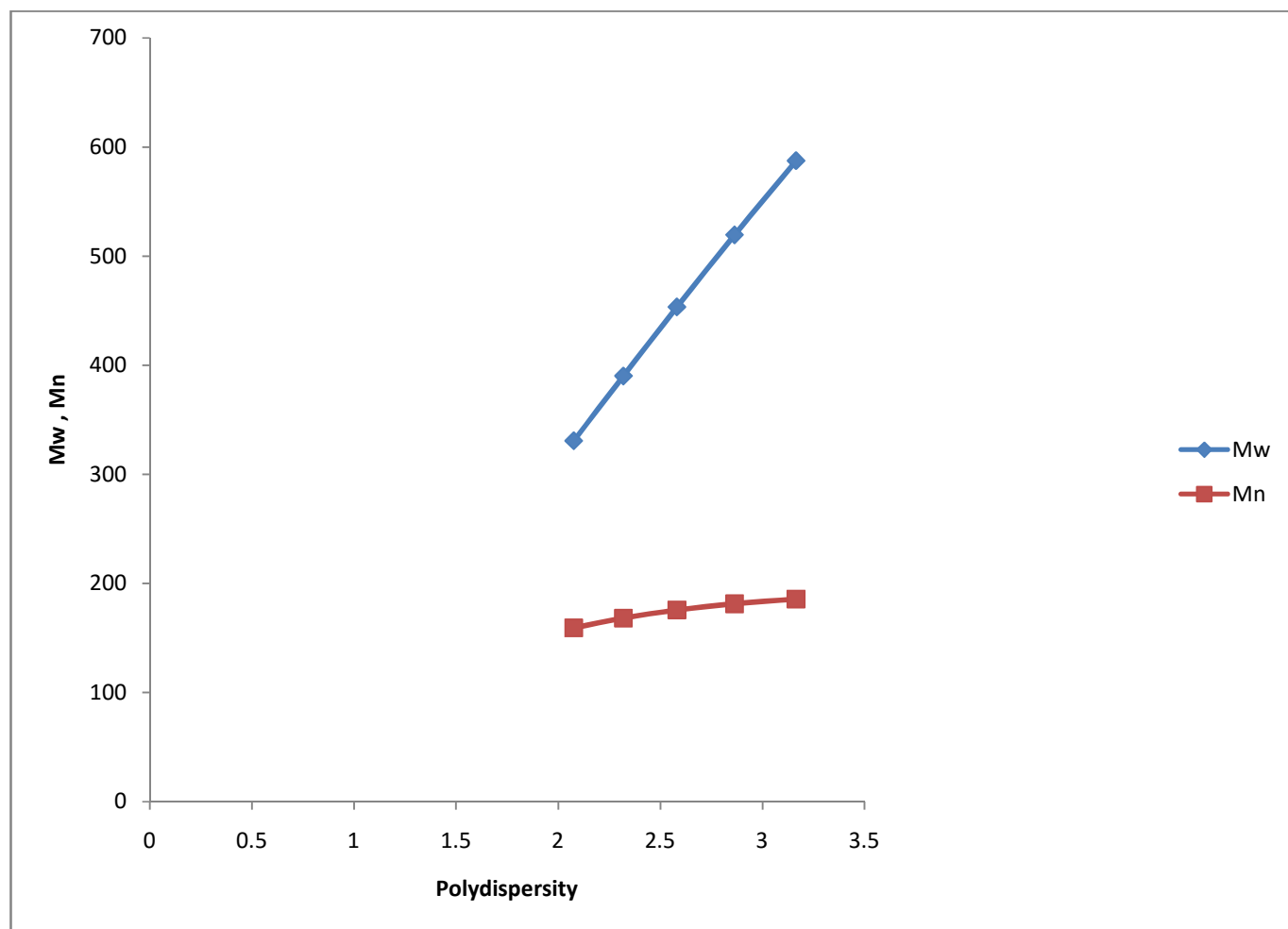


Figure 26: Plot of M_w / M_n versus PDI

4.8. Development of Regression Model

One other core focus in this study is to synthesize PS of required end use property at optimum reaction time, temperature and initiator concentration. Table 14 describes the design of 20 experimental runs carried out. The runs were randomized to minimize the effects of unexpected variability in the experimental responses (styrene monomer conversion). This methodology allows for the formulation of a second-order polynomial equation that describes the process (Eq. 93) for coded and (Eq. 94) for uncoded where X_1 , X_2 and X_3 are the independent variables: reaction temperature, initiator concentration and reaction time, respectively and associated with them are their linear, quadratic and interactive coefficients which indicates their degree of contribution to the dependent variable (% conversion). The observed monomer conversions for the 20 experimental runs are presented in Table 14. These data were used to determine the coefficient of the polynomial equation as earlier explained in Section 3.11. A critical study of Table 14 shows that for conversion, the optimum process variables were found to be a temperature of 120 °C, 0.113 mol/L initiator concentration and 30 minutes reaction time. These estimated coefficients for both the coded and actual values are shown in Table 40 along with the coefficient of determination R^2 , adjusted R^2 , and predicted R^2 . The quadratic models in terms of coded and actual value of variables are shown in Eqs. (93) and (94), respectively.

$$Y = 48.2265 + 11.1217X_1 + 7.6016X_2 - 1.4716X_3 + 3.9144X_1^2 - 0.9223X_2^2 + 1.6905X_3^2 - 0.2750X_1X_3 - 0.4425X_2X_3 + 2.5925X_1X_2 \quad (93)$$

$$Y = 53.2398 - 0.619582 X_1 + 188.92 X_2 - 0.395978 X_3 + 0.00434928 X_1^2 - 962.788 X_2^2 + 0.00422626 X_3^2 + 2.7921 X_1X_2 - 0.000458333 X_1X_3 - 0.714863 X_2X_3 \quad (94)$$

The positive signs in the models signify synergetic effects of factor while the negative sign indicates antagonistic effect. The analysis of variance (ANOVA) of the regression model (Table

38) showed value of $R^2 = 0.9681$, indicating that the model can explain 96.81 % of the data variation and only 3.19 % of the total variations were not explained by the model. For a model to be adequate, value of R^2 should not be less than 0.75 (Le Man *et al.*, 2010). Koocheki *et al.*, (2009) however posited that a large value of R^2 does not always imply that the regression model is a good one and such inference can only be made based on a similarly high value of adjusted R^2 . The value of the adjusted determination coefficient (Adjusted $R^2 = 0.9394$) therefore confirmed that the model was highly significant, which indicated good agreement between the experimental and predicted values of monomer conversion. Thus the model is adequate for prediction in the range of experimental variables. According to Rai *et al.*, (2016), adjusted R^2 and predicted R^2 should be within 20 % to be in good agreement. This requirement is satisfied in this study with a predicted R^2 value of 0.7630. The model therefore offers 76.3 % variability in prediction of monomer conversion beyond the experimental range of process conditions. Table 40 shows the ANOVA of each term of the quadratic model. A term is significant if the F-value is large and $P < 0.05$. From the table, the linear terms X_1 and X_2 are significant, only one quadratic term X_1^2 and one interaction term X_1X_2 are significant. The other terms have no significant effect on monomer conversion. Temperature seems to be the main significant factor as it appears very significant as a linear term, quadratic term and interactive term with initiator concentration.

Table 38: Coefficient of the model

Factor	Coefficient	
	Coded	Uncoded (Actual)
Constant	48.2265	53.2398
X_1	11.1217	-0.619582
X_2	7.6016	188.92
X_3	-1.4716	-0.395978
X_1^2	3.9144	0.00434928
X_2^2	-0.9223	-962.788
X_3^2	1.6905	0.00422626
X_1X_3	-0.2750	-0.000458333
X_2X_3	-0.4425	-0.714863
X_1X_2	2.5925	2.79214
R-square	96.81%	
Adjusted R-square	76.30%	
Predicted R-square	93.94%	

Table 39: Analysis of variance (ANOVA) for response surface quadratic model

Source	Sum of squares	DF	Mean square	F-value	T-value	P-value
Regression model	2839.34	9	315.48	33.74	38.673	0.000
Linear	2507.97	3	835.99	89.42	13.442	0.000
X_1	1689.25	1	1689.25	180.69	9.187	0.000
X_2	789.15	1	789.15	84.41	-1.779	0.000
X_3	29.57	1	29.57	3.16		0.106
Square	275.42	3	91.81	9.82	4.860	0.003
X_1^2	233.57	1	220.81	23.62	-1.145	0.001
X_2^2	12.26	1	12.26	1.31	2.099	0.279
X_3^2	29.60	1	41.18	4.41		0.062
Interaction	55.94	3	18.65	1.99	-0.254	0.179
X_1X_3	0.60	1	0.60	0.06	-0.409	0.802
X_2X_3	1.57	1	1.57	0.17	2.398	0.691
X_1X_2	53.77	1	53.77	5.75		0.037
Residual error	93.49	10	9.35			
Lack of fit	90.89	5	18.18	34.95		
Pure error	2.60	5	0.52			
Total	2932.83	19				

Earlier, we mentioned that kinetic modeling of the free radical polymerization is characterized by intricacies, inaccuracies and mathematical rigors which render its routine usage especially in practice a serious challenge. Rate parameters (rate constants) of the elementary steps are not easy to determine. The classical steady state approximation fails to provide accurate results especially at high conversion owing to increased viscosity of the reaction mixtures. All these either reduce the reliability of the kinetic model or make its use very cumbersome. The statistical models however offers advantage in this regard, even as it saves time, energy and resources since it uses just only the operating or process conditions only to predict the styrene conversion. The recent data of Mermier *et al.*, (2015), were used to test the predictive capacity of the statistical model as shown in Figures 27 to 29 with good degree of accuracy. Figure 30 shows the plot of predicted conversion by the developed model against experimental values. The model successfully captured the correlation between the process conditions and monomer conversion because the predicted values were very close to the observed values.

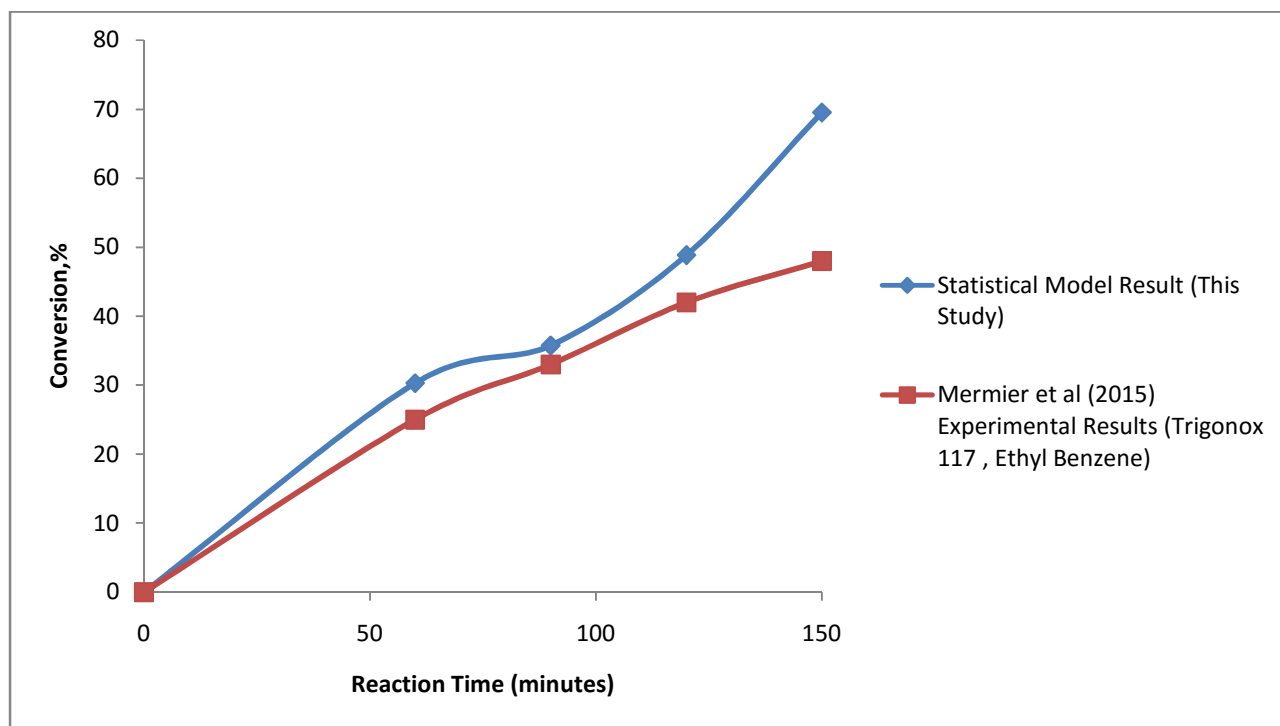


Figure 27: Comparison of experimental data with modeled result at 120 °C and 1.3 mmol initiator concentration.

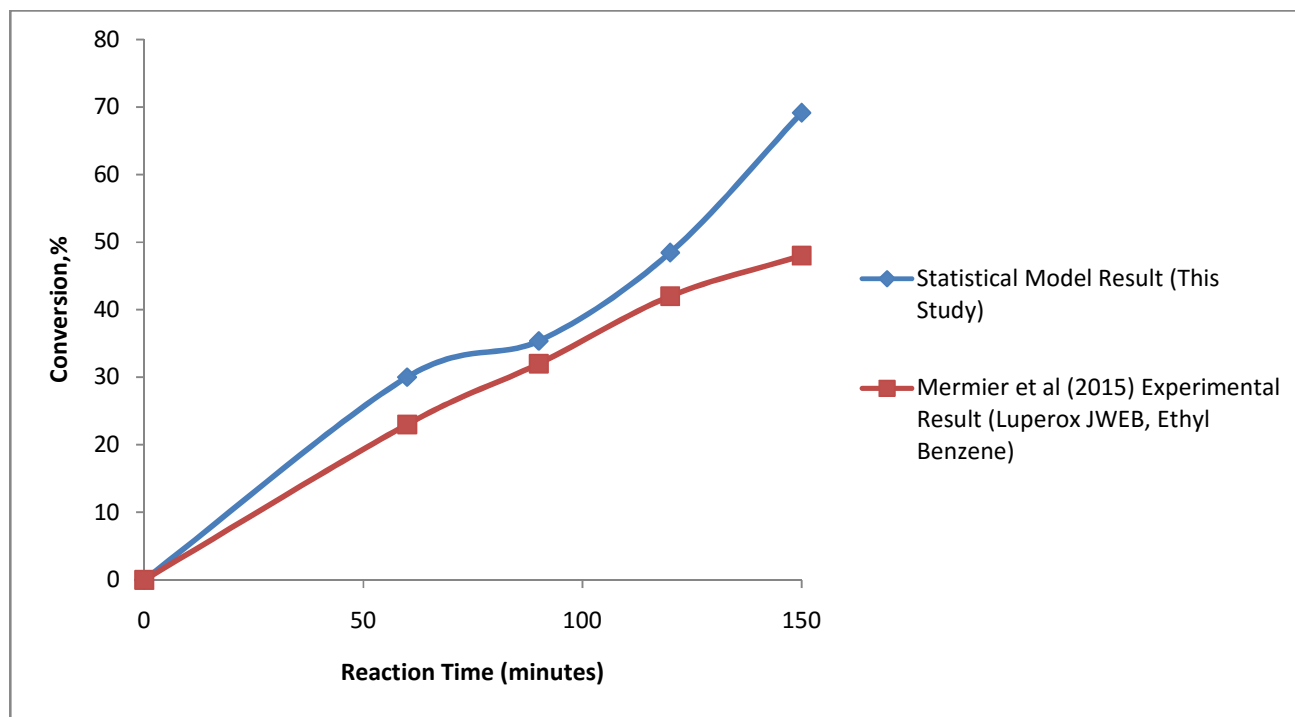


Figure 28: Comparison of experimental data with modeled result at 120 °C and 0.38 mmol initiator concentration.

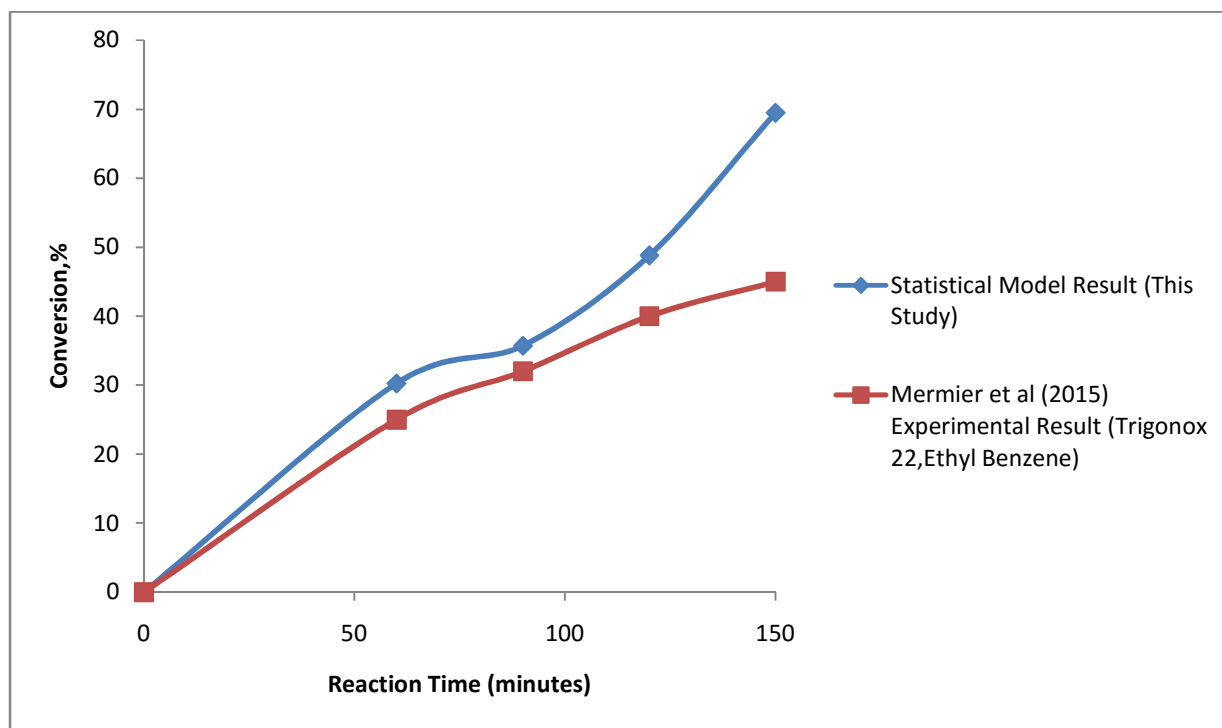


Figure 29: Comparison of experimental data with modeled result at 120 °C and 1.2 mmol initiator concentration.

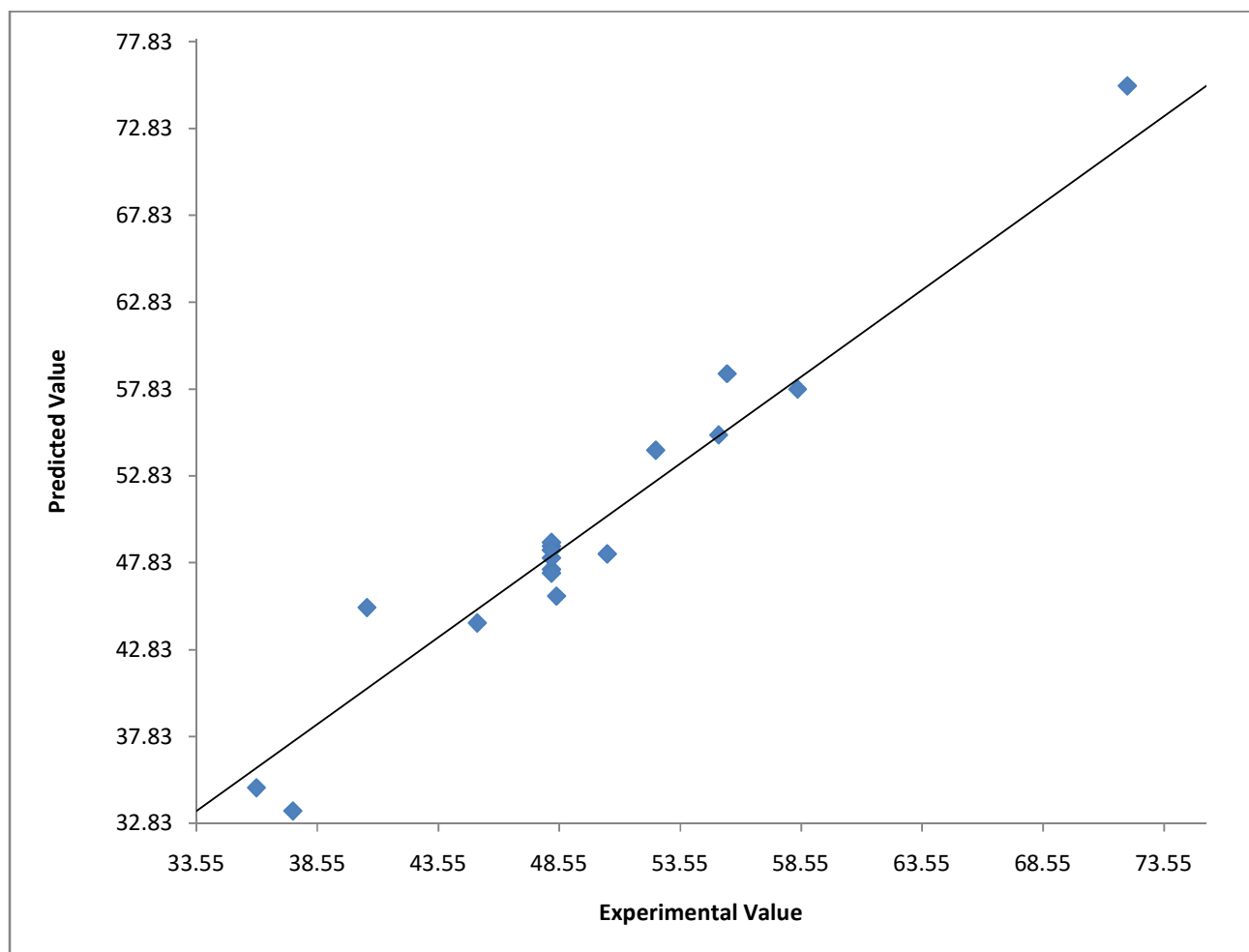


Figure 30: Variation of % conversion of styrene monomer observed in the experiment with predicted values by the model.

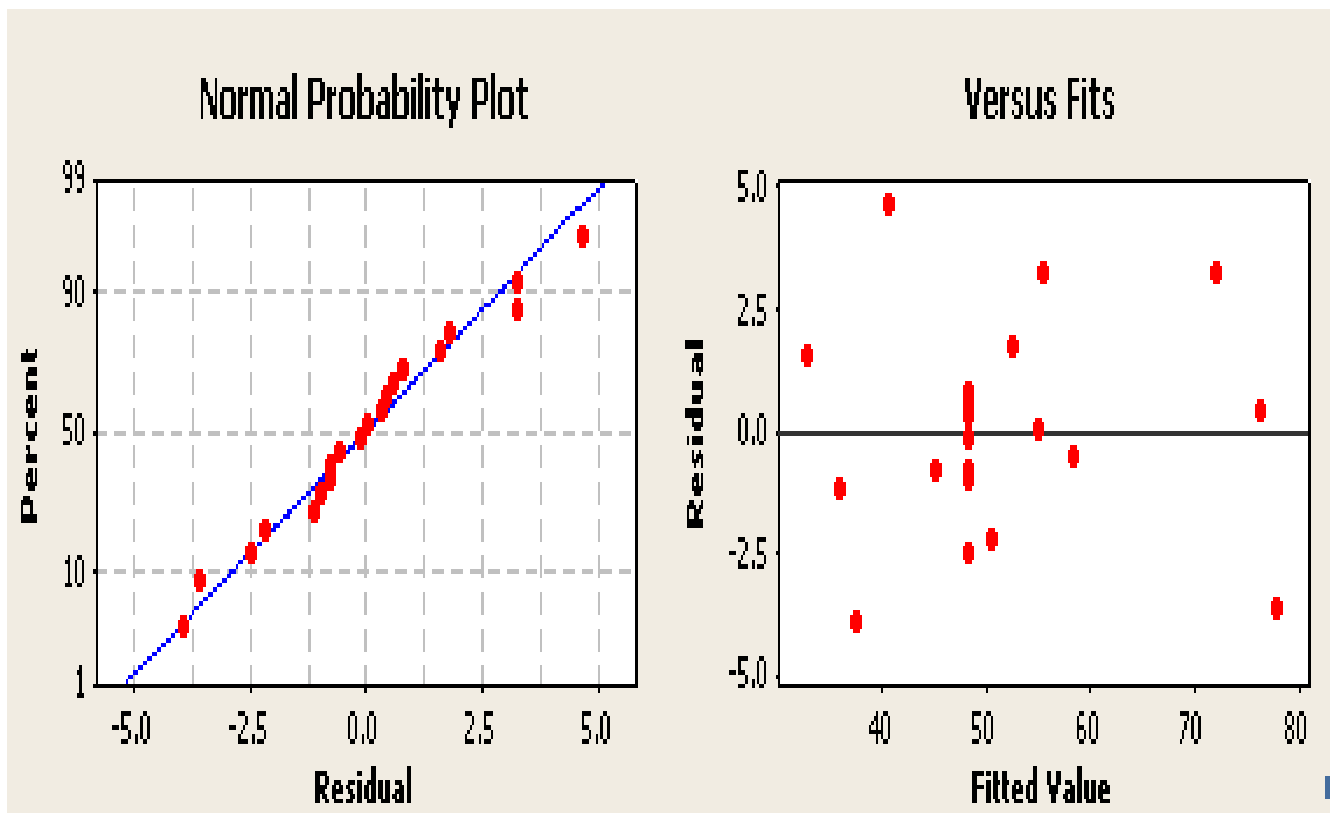


Figure31:Normal Probability Plot of the Residuals Figure 32: Plot of Residual versus Predicted Response

The adequacy of the model has also been investigated by examination of the residuals as described by Chieng *et al.*, (2012). Figures 31 and 32 have been used to examine the residuals which is the difference between the respective observed response and the predicted response. If the model is adequate, Figure 30 should form a straight line. A check on the plot shows that the residuals generally fall on a straight line which implies that the errors are distributed normally. Figure 32 shows that all experimental data points are uniformly distributed around the mean of the response variable. The residual are quite fairly symmetrical and there is no significant heteroscedasticity. All these imply that the model proposed is adequate.

4.9. Analysis of Response Surface

Three-dimensional response surfaces were plotted to investigate the interaction between the variables and to determine the optimum condition of each factor for maximum styrene conversion. The effect of initiator concentration and reaction temperature on styrene conversion at a constant reaction time of 50 min is presented in Figure 33. As the reaction temperature and initiator concentration increase, the styrene monomer conversion increases. Maximum styrene conversion was obtained at initiator concentration of 0.1346 mol/l. The optimum styrene conversion could be obtained at about 120 °C and initiator concentration of 0.1346 mol/l. Overall, there is a net positive interactive effect between the two process variables. This is a strong indication of the dependence of the styrene monomer conversion on both the temperature and initiator concentration. This obviously follow the Arrhenius law since styrene conversion increases for the same reaction time at higher temperatures.

Surface Plot of % Conversion vs Initiator concentration, Reaction Temp.

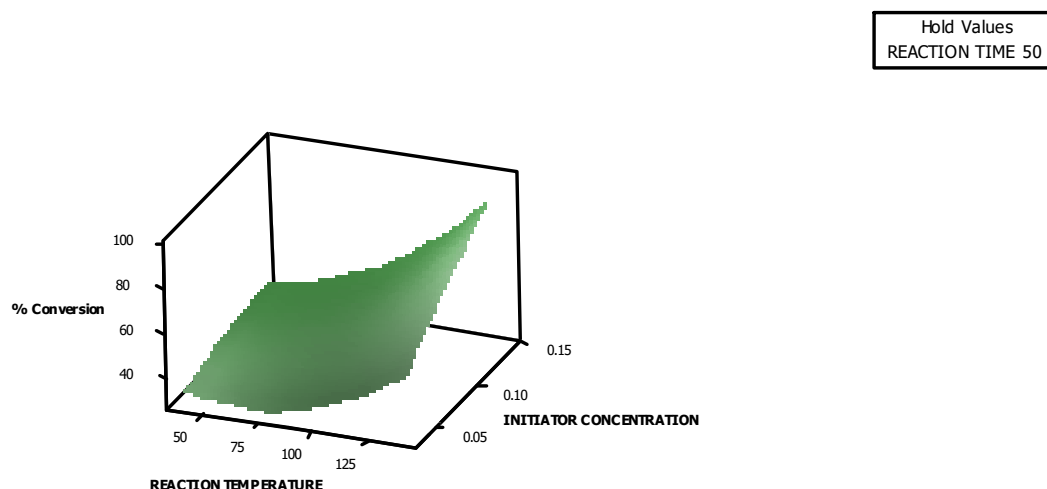


Figure 33: Response surface plot of the interactive effect of initiator concentration and reaction temperature on % styrene conversion holding reaction time constant

The interactive effects of initiator concentration and reaction time on styrene conversion at a constant reaction temperature of 90 °C are shown in Figure 34. The conversion was observed to rapidly increase with increase in initiator concentration compared to that of reaction time. There is a negative significant interaction between the initiator concentration and reaction time. This shows that the styrene conversion reduces with increase in initiator concentration and reaction time. There is probably an indication of lower solvent cage effect below this temperature at particular reaction time which allows the generated radicals to escape into the bulk medium and grow.

Surface Plot of %Conversion vs Initiator concentration, Reaction time.

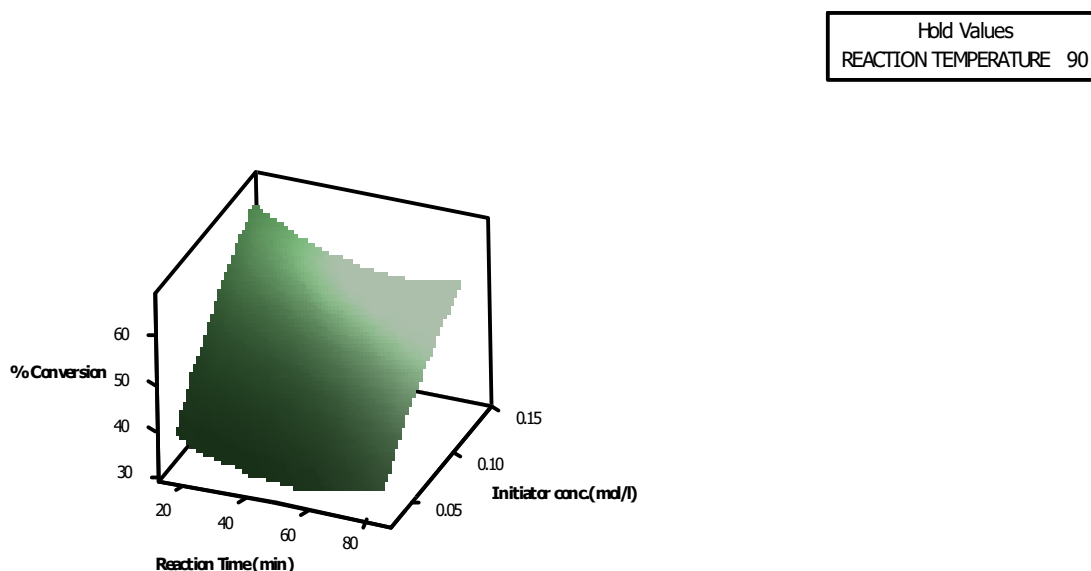


Figure 34: Response surface plot of the interactive effect of initiator concentration and reaction time on % styrene conversion holding reaction temperature constant

The plot in Figure 35 is similar to that of Figure 34. The interactive effect of reaction temperature and reaction time on styrene conversion at a constant initiator concentration of

0.0825 mol/l is shown in Figure 35. The conversion was observed to rapidly increase with increase in reaction temperature compared to that of reaction time. There is a negative significant interaction between the reaction temperature and reaction time. This shows that the styrene conversion reduces with increase in reaction temperature and reaction time above the optimum value of 0.0825 mol/l initiator concentration.

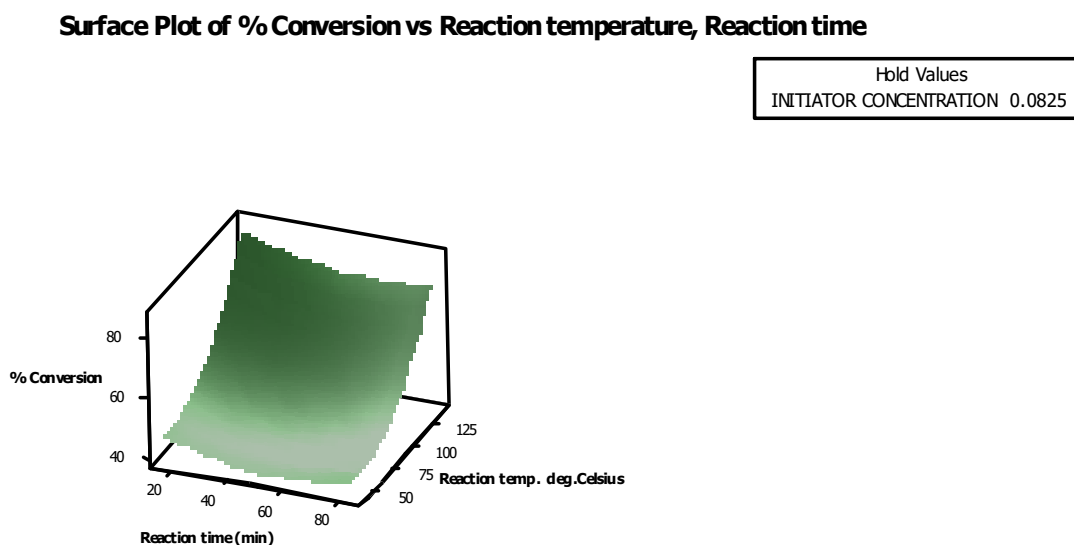


Figure 35: Response surface plot of the interactive effect of reaction temperature and reaction time on % styrene conversion holding initiator concentration constant.

Figure 36 shows the contour plots of styrene conversion as a function of reaction temperature and time. It can be seen that increase in temperature and lower reaction time (between 20 to 30 minutes) would increase the styrene conversion. This may be due to the formation of radical population at the early period of the reaction. Specifically, a conversion of above 80 %, between 70-80 %, 60-70 %, 50-60 % and less than 50 % are obtainable at reaction temperatures of 140, 120, 100 and 72 °C, respectively at a constant initiator concentration of 0.0825 mol/l. The reaction temperature and reaction times demonstrated a suppressive effect on each other.

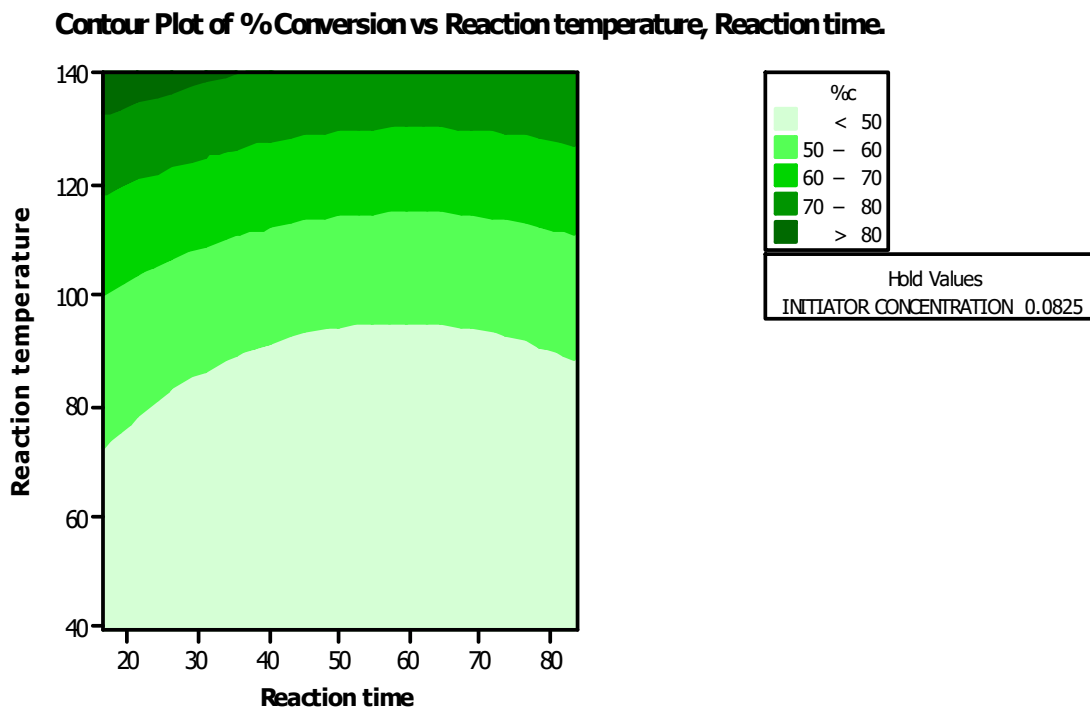


Figure 36: Contour plot of % conversion with reaction temperature and reaction time.

Figure 37 shows the contour plots of styrene conversion as function of initiator concentration and reaction time. From the plots, operating at high initiator concentration and low reaction time as experienced in earlier case is favourable to increase conversion while holding temperature at 90 °C. A suppressive effect or interplay was also observed by the two process variables (initiator concentration and reaction time). Least conversion of less than 35 % conversion is obtainable at operating conditions 30 to 75 mins reaction time, 0.04 mol/l initiator concentration and 90 °C .

A synergetic effect of process variables (initiator concentration and reaction temperature) was observed in Figure 38. High styrene conversion (greater than 90 %) is obtained at higher reaction time and higher initiator concentration while low styrene conversion happens (less than 35 %) at reversed operating conditions.

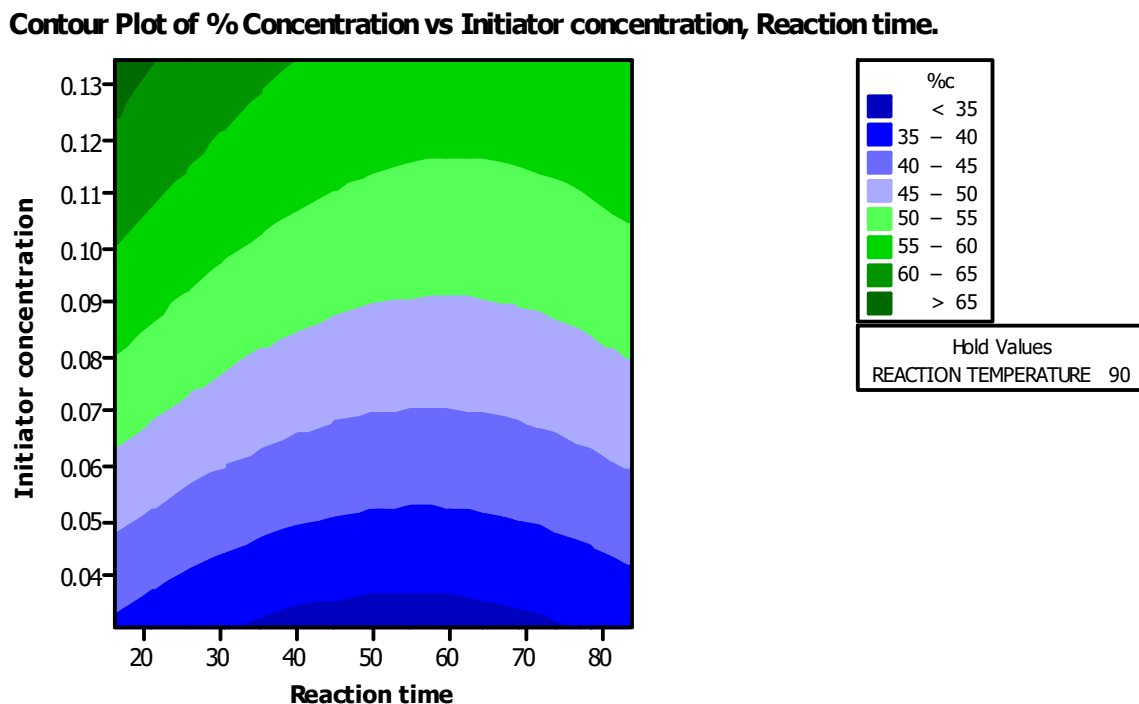


Figure 37: Contour plot of % conversion with initiator concentration and reaction time.

Contour Plot of % Conversion vs Initiator concentration, Reaction temp.

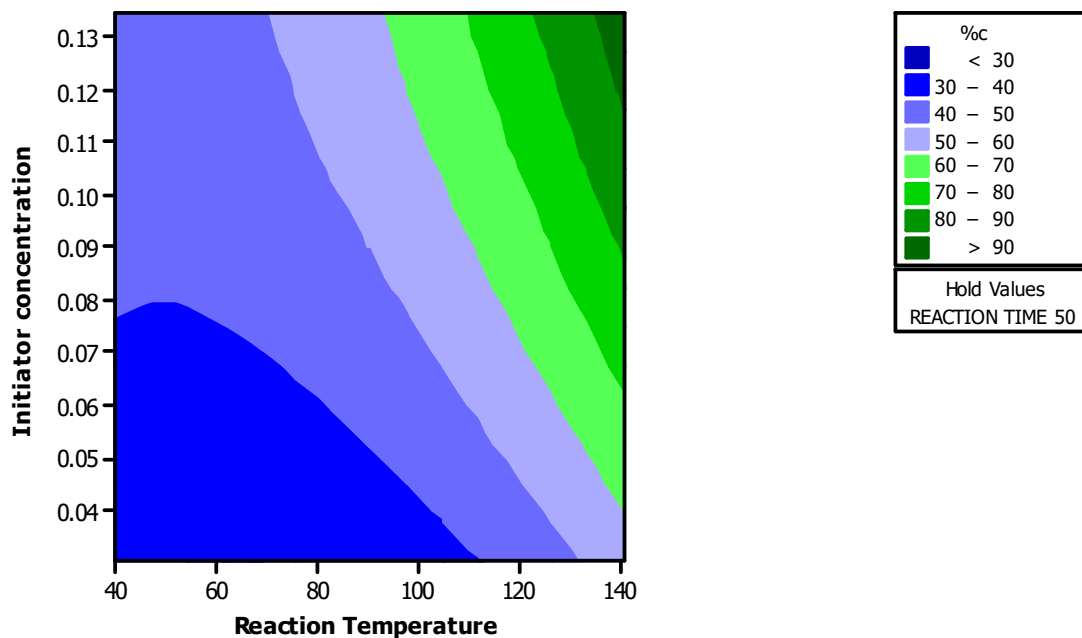


Figure 38: Contour plot of % Conversion with Initiator Concentration and Reaction Temperature.

4.10. Optimization and Validation

In order to obtain the maximum response that jointly satisfy all process conditions, optimization was carried out using the RSM software (MINITAB Version 16.0). The optimum conditions obtained from this study are as follows: reaction time of 30 min, reaction temperature of 120 °C and initiator concentration of 0.1135 mol/l. The corresponding optimized monomer conversion is 76.82 %. Validation experimental runs were conducted using the optimum conditions in duplicate and the average value of conversion obtained is 70.86 %. In comparison with the predicted value, there is an error of about 8.41 %. There is therefore a good agreement between the experimental value and the predicted value based on the model. It is also pertinent to state that the optimized conversion obtained in this study is remarkably comparable with a conversion

of 70 % at a similar temperature of 120 °C reported to be common in industrial sites for production of general purpose polystyrene resins (Mermier *et al.*, 2015).

4.11. Characterization of the Polystyrene

The polystyrene sample prepared with optimum conditions was subjected to few analyses and the findings are presented and discussed in this section.

4.11.1. Spectral Analysis

The Infra-Red (IR) was used to characterise the synthesized PS. The spectral of the optimized sample and another sample prepared by bulk polymerization are shown in Figures 39 and 40, respectively. The aromatic ring and alkene that characterize polystyrene dominates the spectrogram (1448.74-1695.18 cm^{-1}). This is more apparent when the sample spectrals (Figures 39 and 40) are compared with the reference (Figure 41). The peaks at 1599.01 and 1448.74 cm^{-1} are assigned to C=C stretching of phenyl group. The C-H deformation vibration band of benzene ring hydrogen was seen at 751.64 cm^{-1} and ring deformation was observed at 693.61 cm^{-1} (Naghash *et al.*, 2007; Kaniappan and Latha, 2011). This confirmed that the PS retained the benzene ring of the styrene from which it was formed. Both the reference and Samples spectrogram are almost identical in peak position and intensity (Table 40) excluding the peak above 3500 cm^{-1} in the samples spectra probably due to the presence of minor foreign materials. The spectral obtained from sample synthesized through the bulk approach (industrial method) (Figure 40) is very similar with that of the solution polymerization approach (Figure 39). This is an indication that the introduced solvent (acetone) did not distort the end composition of the PS.

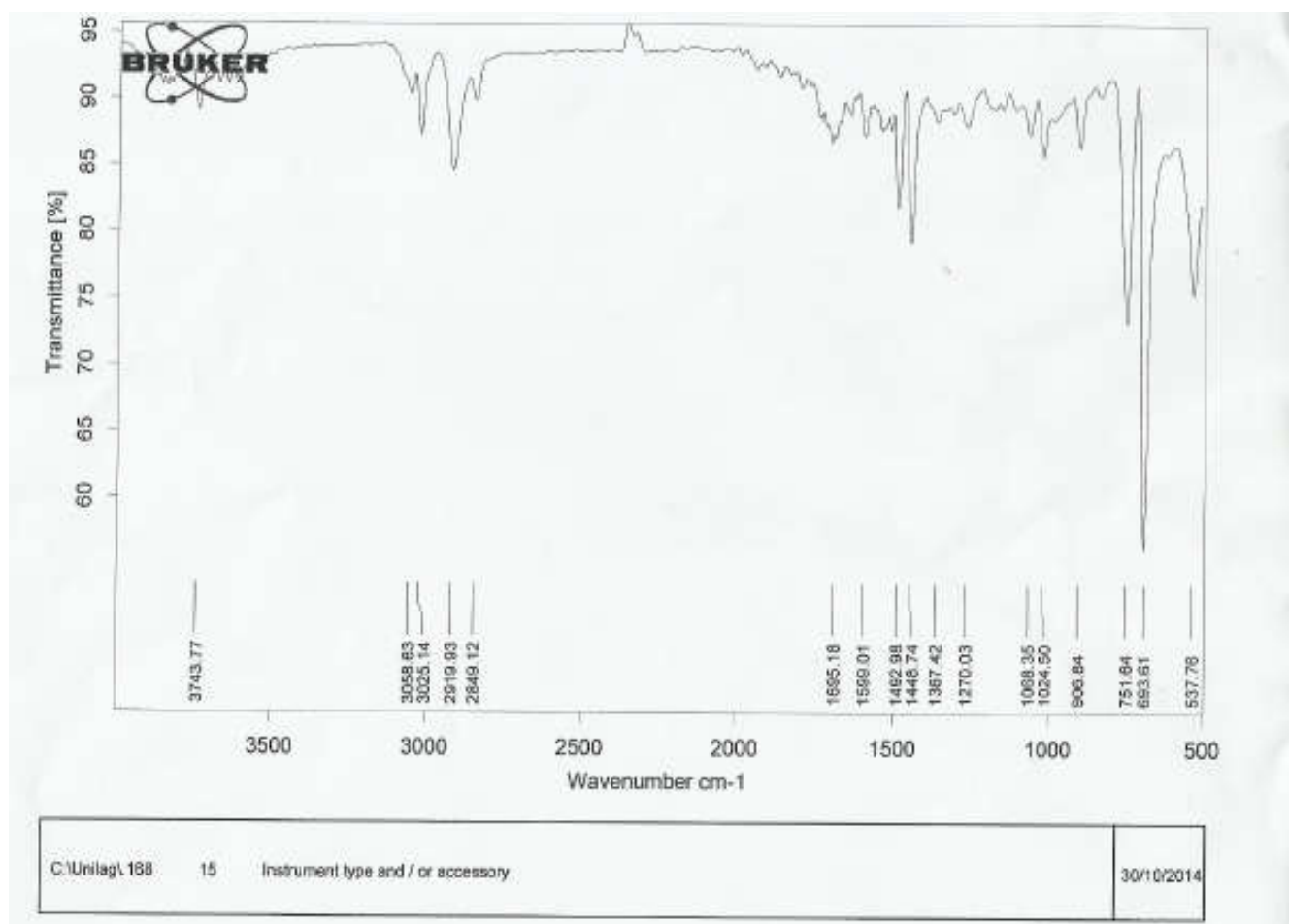


Figure 39: Infra-red spectral of PS obtained through the optimized process conditions

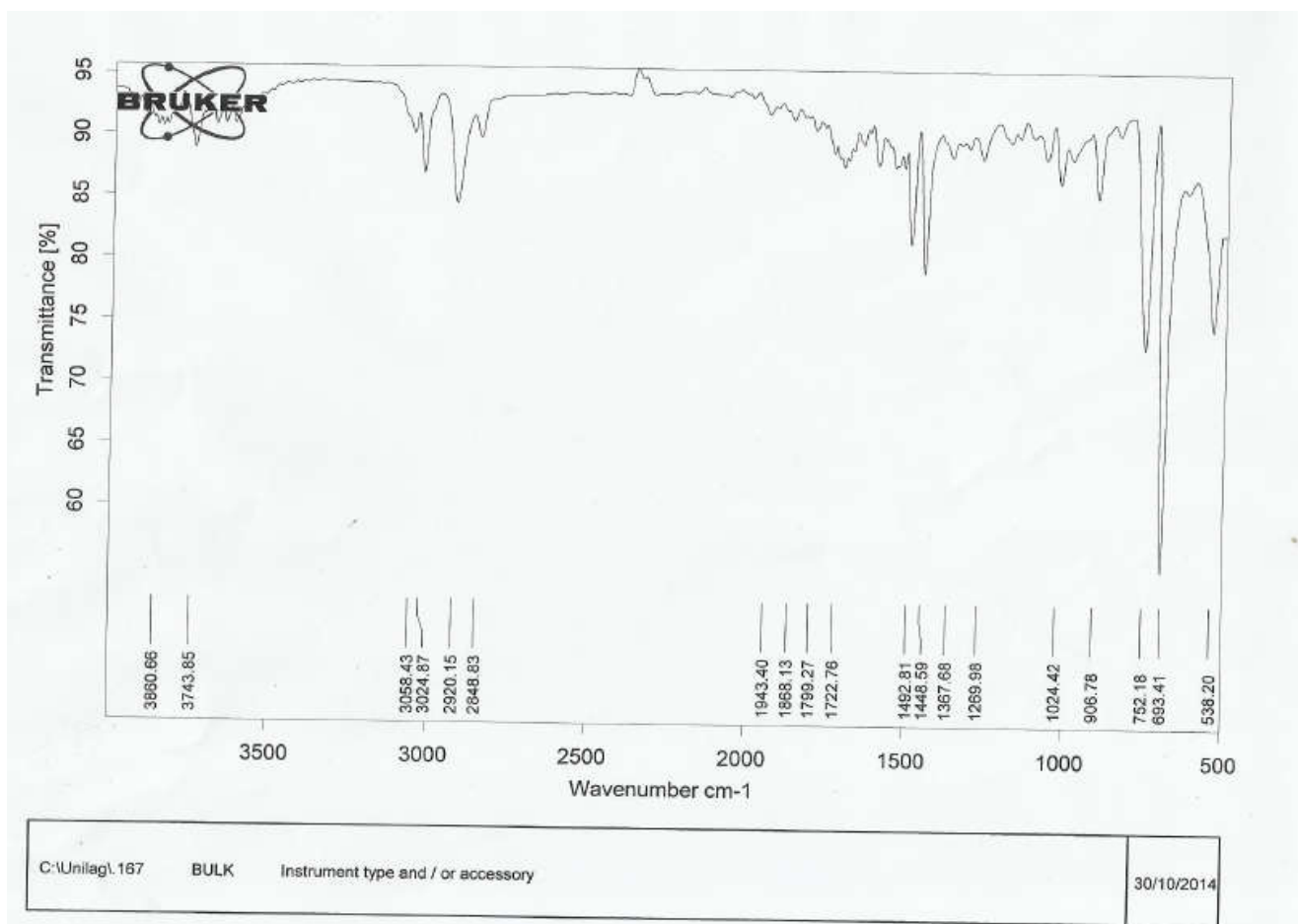


Figure 40: Infra-red spectral of PS obtained by bulk polymerization approach.

Table 40: Polystyrene major peaks

S/N	Wave numbers in cm^{-1} (Nicholas, 2012)	Wave numbers in cm^{-1} (This study)
1.	538.8	537.76
2.	623.3	693.61
3.	694.1	---
4.	752.1	751.64
5.	905.9	906.84
6.	966.4	---
7.	1025.7	1024.50
8.	1068.4	1068.35
9.	---	1270.03
10.	1367.6	1367.42
11.	1448.8	1448.74
12.	1491.0	1492.98
13.	1599.3	1599.01
14.	---	1695
15.	2849.9	---
16.	2920.1	2849.12
17.	---	2919.93
18.	3024.9	3025.14
19.	3059.5	3058.63
20.	---	3743.77

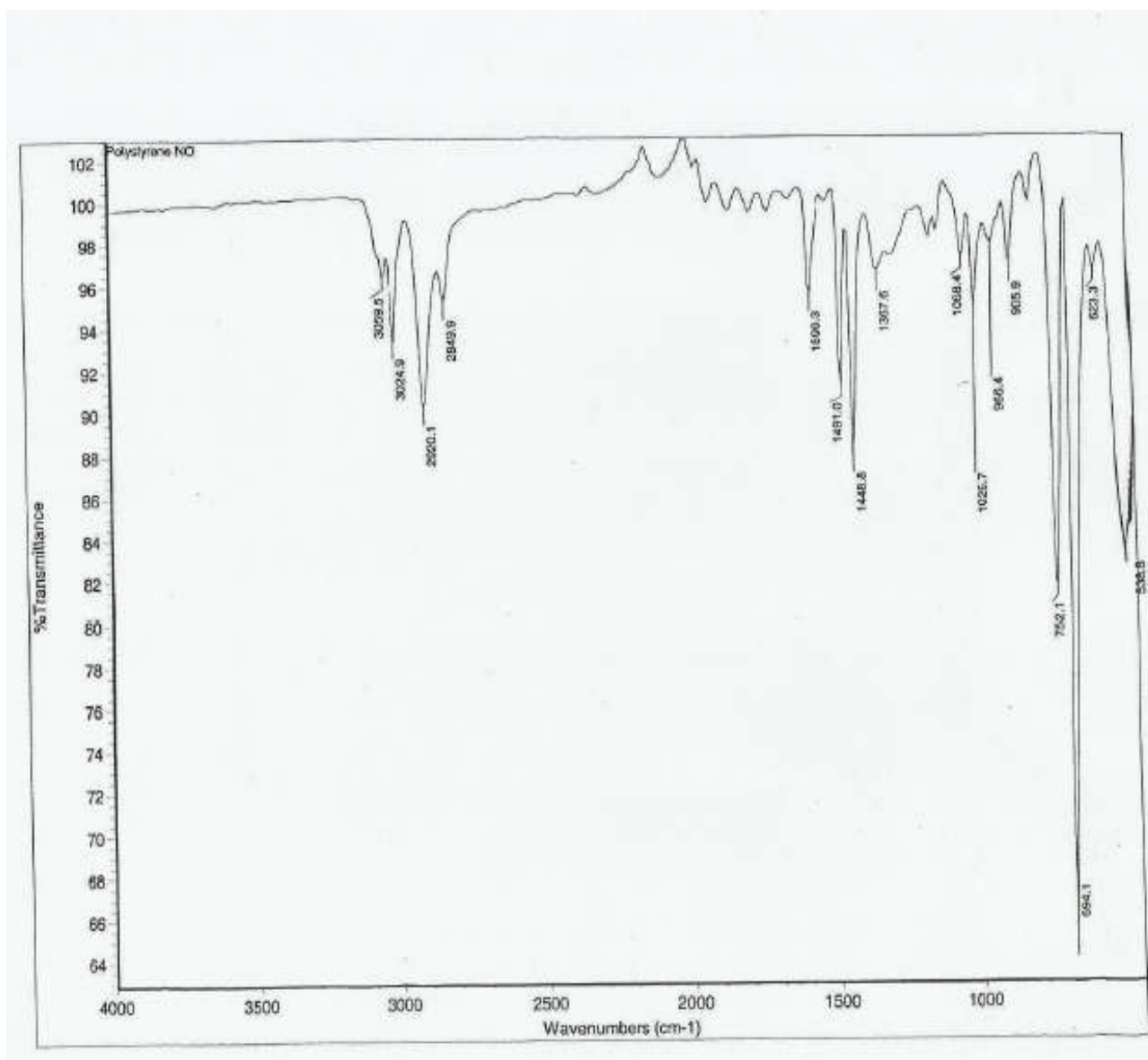


Figure 41: Reference spectra for polystyrene (Nicholas, 2012)

4.11.2. Molecular weight

The molecular weight of the optimized sample was determined through viscosity measurement. The value obtained was 5.65738×10^5 . When compared with recommended values ($5.5 - 20.5 \times 10^5$) reported by Wagner (1985) and Goldberg et al. (2003). The value is within acceptable range hence ensures easy processability. The optimized sample therefore has useful commercial applications and the ability to bear sufficient design loads.

4.11.3. Melting point of PS

Bindul *et al.*, (2001) linked the melting point of materials to its thermal property. Park *et al.*, (2001) similarly related melting point of polymers to their molecular weights, degree of cross linking and polymer rigidity. Materials with sharp melting points exhibit sound thermal, morphological and molecular properties. The melting point of optimized sample in this study was determined to be in the range of 215-220 °C. This is slightly different from values reported for PS in literature such as 240 °C (Maria *et al.*, 2008), 262.9- 270.1 °C (Chen *et al.*, 2009) and 275 °C (Brun *et al.*, 2011). As observed in the spectral analysis (Figures 39 and 40), the reduced melting point in this study may be as a result of foreign bodies likely to be present in the PS (as evidenced by Peak 3500 cm^{-1} on the spectrogram). However, the wide disagreement in the melting points of PS obtained by Maria *et al.*, (2008) with others is due to the nature of PS formed in each case. The later synthesized ordered syndiotactic polystyrene (through Ziegler – Natta polymerization) with the phenyl groups positioned on alternating sides of the hydrocarbon backbone. This form is highly crystalline with a T_m of 270 °C (518 °F). Such PS is not commercially produced because the polymerization is slow. The former performed similar polymerization though under different control and activation environments.

4.11.4. Chemical Resistance Evaluation

The results of the chemical resistance test carried out under laboratory condition are as presented in Table 45. The test is to actually rationalize the likely changes such as swelling, change in mass or appearance the PS may experience due to interaction with some solvents.

Table 41: Chemical resistance evaluation at room temperature

Solvents	DS (%)after			State of PS
	24 hrs	48 hrs	72 hrs	
Water	17.14	21.88	15.79	Still remain solid and hard
Ethanol	03.51	04.76	10.17	Still remain solid and hard
Tetrahydrofuran	Complete dissolution			Dissappeared

DS = Degree of swelling = $(M_2 - M_1) * 100 / M_1$ Sani *et al.* (2006)

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1. Summary of Findings

Table 42: Table of Findings

S/N	Objectives of the work	Findings of the work
1.	To investigate the compatibility of solvents and initiators in the styrene monomer polymerization (solution polymerization) in a bid to achieve a safe polymerization process coupled with the determination of the link between solvent properties / solvatochromic parameters on polymerization rate and styrene monomer conversion.	Acetone has been shown to be a good solvent for styrene polymerization based on monomer conversion and thermodynamic requirement in terms of ease of separation of the polymer-solvent solution. Its ready solubility with the known industrial initiator (BPO) and its relatively green nature (GRASS) in terms of physico-chemical properties and method of preparation further enhanced its optimum properties for the entire polymerization process. Further more, The order of monomer conversion as obtained in this work is as follows: acetone > ethylacetate > chloroform > DMSO > acetonitrile > benzene > toluene. This arrangement is not according to their degree of polarity. This suggests interplay of other contributory factors especially at the molecular level. Multiparameter correlation through the linear solvation energy relationship show that for BPO initiator, dipolarity/polarizability and Reichardt electrophilicity have positive effect on styrene monomer conversion. Therefore, heuristic of increasing solvent polarity to achieve more styrene monomer conversion is not always quantitatively valid.
2.	To investigate the vinyl monomer polymerization using green engineering approach i.e. the use of biodiesel in the polymerization.	Biodiesel solvents gave much lower styrene monomer conversion when compared to the other organic solvents. It was tagged bio-solution polymerization in this study. WCOB gave a higher conversion when compared to PSOB for each of the

		initiators at higher temperature (120 °C) but gave approximately similar styrene monomer conversion at lower temperatures (60 and 90 °C).
3.	To develop a free radical kinetic model for the prediction of styrene monomer conversion with time of the polymerization and estimation of polydispersity index.	A kinetic model was developed capable of predicting styrene monomer conversion at different operating conditions. The Garg approach was adopted for the estimation of PDI.
4.	To carry out optimization studies of the styrene polymerization in solvent media using the response surface methodology (RSM) and the development of models in terms of process parameters.	A robust statistical model for predicting monomer conversion was developed based on process parameters via response surface methodology. The developed model obviates the inaccuracies and complexity typical of kinetics based model. The effects of process variables on solution polymerization of styrene individually and interactively have been estimated. The optimum process variables to obtain maximum styrene conversion was achieved at temperature (120 °C), initiator concentration (0.113 mol/L) and reaction time (30 mins) to obtain an average of 76.82 % styrene monomer conversion base on the parameters considered in this study.
5.	To characterize the synthesized polystyrene at optimum conditions.	The synthesized polystyrene at optimum conditions were all found to meet required industrial specification.

5.2 Conclusion

In conclusion, acetone has been identified as a good solvent for styrene polymerization based on styrene monomer conversion and ease of PS separation. Therefore, it is the recommended solvent, rather than the commonly used toluene, as solvent for styrene polymerization.

Similarly, in the study, biodiesel solvents gave lower styrene monomer conversion compared to molecular solvents; it is still instructive to note that they remain a promising green solvent for styrene polymerization in future. The study reveals a very strong influence of solvent polarity on styrene monomer conversion in the solution polymerization of styrene. Multiparameter correlation through the linear solvation energy relationship show that for BPO initiator (industrially used initiator), dipolarity/polarizability and Reichardt electrophilicity have positive effect on styrene monomer conversion, while refractive index, acidity, and basicity are the main negative contributors. The heuristic of increasing solvent polarity to obtain a high styrene monomer conversion is therefore not always quantitatively valid. Three styrene monomer conversion models were developed; kinetic model, and statistical models in terms of both solvatochromic parameters and process parameters. The process parameters model was found to be a robust model for predicting styrene monomer conversion and highly suitable for routine industrial application. The model therefore obviates the inaccuracies and complexity typical of kinetics based model.

5.2. Contributions to Knowledge:

- i. Acetone has been identified as a good solvent for styrene polymerization in terms of styrene monomer conversion and ease of product separation.
- ii. A statistical model in terms of solvatochromic parameters that influence chemical character of solvent and conversion of styrene into polystyrene has been established for the first time. Similar model for predicting monomer conversion was also developed based on kinetic parameters.
- iii. A robust model for predicting monomer conversion suitable for routine industrial application was developed based on process parameters via response surface methodology thereby obviating the inaccuracies and complexity of kinetics based model.
- iv. Bio – solvent such as biodiesel has also been found to be a promising green solvent for styrene polymerization in future.

5.3. Recommendations

- i. In a bid to ensure green chemical process and product of specific properties, polymerization of styrene in other green solvents such as ionic liquids is recommended
- ii. Polymerization initiators are expensive, the search for an alternative from local source is recommended.
- iii. No polystyrene plant exists in Nigeria; as a result, the process engineering design aspect for large scale production of polystyrene is recommended in future studies.

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45.	2SA16	STYRENE(1):ACETONE(2)	5.1	20.60	50	80.57	0.231
46.	2SC16	STYRENE(1):CHLOROFORM(2)	4.1	4.81	50	56.73	0.163
47.	3SA17	STYRENE(1):ACETONE(3)	5.1	20.60	50	21.63	0.062
48.	3SC17	STYRENE(1):CHLOROFORM(3)	4.1	4.81	50	21.63	0.062
49.	4SA18	STYRENE(1):ACETONE(4)	5.1	20.60	50	22.28	0.064
50.	4SC18	STYRENE(1):CHLOROFORM(4)	4.1	4.81	50	20.97	0.060

a =David (1995) , b = Michael and Irene (2003)

Table 44: Effect of Polarity Index (P.I)/ Dielectric Constant (c) of Solvents on Rate of Polymerization (Rp) and Monomer Conversion(x) using BPO Blend

S/N	SAMPLES	STYRENE: SOLVENTS	P.I ^{a,b}	ε ^{a,b}	TIME MIN	X (%)	$R_p = \frac{d[p]}{dt} \left\{ \frac{Mol}{l.s} \right\} 10^{-2}$
1.	1SA11	STYRENE(1):ACETONE(1)	5.1	20.60	10	82.78	1.188
2.	1SC11	STYRENE(1):CHLOROFORM(1)	4.1	4.81	10	49.67	0.713
3.	1SB11	STYRENE(1):BENZENE(1)	2.7	2.30	10	39.07	0.561
4.	1ST11	STYRENE(1):TOLUENE(1)	2.4	2.38	10	15.23	0.219
5.	2SA12	STYRENE(1):ACETONE(2)	5.1	20.60	10	57.62	0.827
6.	2SC12	STYRENE(1):CHLOROFORM(2)	4.1	4.81	10	48.57	0.697
7.	3SA13	STYRENE(1):ACETONE(3)	5.1	20.60	10	59.38	0.852
8.	3SC13	STYRENE(1):CHLOROFORM(3)	4.1	4.81	10	43.71	0.627
9.	4SA14	STYRENE(1):ACETONE(4)	5.1	20.60	10	22.30	0.320
10.	4SC14	STYRENE(1):CHLOROFORM(4)	4.1	4.81	10	23.19	0.333
11.	1SA12	STYRENE(1):ACETONE(1)	5.1	20.60	20	87.92	0.631
12.	1SC12	STYRENE(1):CHLOROFORM(1)	4.1	4.81	20	81.68	0.586
13.	1SB12	STYRENE(1):BENZENE(1)	2.7	2.30	20	41.06	0.295
14.	1ST12	STYRENE(1):TOLUENE(1)	2.4	2.38	20	35.76	0.257
15.	2SA13	STYRENE(1):ACETONE(2)	5.1	20.60	20	69.76	0.501
16.	2SC13	STYRENE(1):CHLOROFORM(2)	4.1	4.81	20	68.43	0.491
17.	3SA14	STYRENE(1):ACETONE(3)	5.1	20.60	20	60.49	0.434
18.	3SC14	STYRENE(1):CHLOROFORM(3)	4.1	4.81	20	54.75	0.393
19.	4SA15	STYRENE(1):ACETONE(4)	5.1	20.60	20	23.19	0.166
20.	4SC15	STYRENE(1):CHLOROFORM(4)	4.1	4.81	20	25.61	0.184
21.	1SA13	STYRENE(1):ACETONE(1)	5.1	20.60	30	83.82	0.401
22.	1SC13	STYRENE(1):CHLOROFORM(1)	4.1	4.81	30	73.51	0.352
23.	1SB13	STYRENE(1):BENZENE(1)	2.7	2.30	30	39.29	0.188
24.	1ST13	STYRENE(1):TOLUENE(1)	2.4	2.38	30	36.42	0.174

25.	2SA14	STYRENE(1):ACETONE(2)	5.1	20.60	30	55.41	0.265
26.	2SC14	STYRENE(1):CHLOROFORM(2)	4.1	4.81	30	47.90	0.229
27.	3SA15	STYRENE(1):ACETONE(3)	5.1	20.60	30	34.66	0.166
28.	3SC15	STYRENE(1):CHLOROFORM(3)	4.1	4.81	30	30.91	0.148
29.	4SA16	STYRENE(1):ACETONE(4)	5.1	20.60	30	21.63	0.103
30.	4SC16	STYRENE(1):CHLOROFORM(4)	4.1	4.81	30	24.94	0.119
31.	1SA14	STYRENE(1):ACETONE(1)	5.1	20.60	40	85.48	0.307
32.	1SC14	STYRENE(1):CHLOROFORM(1)	4.1	4.81	40	80.77	0.304
33.	1SB14	STYRENE(1):BENZENE(1)	2.7	2.30	40	42.38	0.152
34.	1ST14	STYRENE(1):TOLUENE(1)	2.4	2.38	40	38.19	0.137
35.	2SA15	STYRENE(1):ACETONE(2)	5.1	20.60	40	55.85	0.200
36.	2SC15	STYRENE(1):CHLOROFORM(2)	4.1	4.81	40	52.54	0.189
37.	3SA16	STYRENE(1):ACETONE(3)	5.1	20.60	40	34.22	0.123
38.	3SC16	STYRENE(1):CHLOROFORM(3)	4.1	4.81	40	30.46	0.109
39.	4SA17	STYRENE(1):ACETONE(4)	5.1	20.60	40	22.52	0.081
40.	4SC17	STYRENE(1):CHLOROFORM(4)	4.1	4.81	40	22.96	0.082
41.	1SA15	STYRENE(1):ACETONE(1)	5.1	20.60	50	85.40	0.245
42.	1SC15	STYRENE(1):CHLOROFORM(1)	4.1	4.81	50	80.65	0.246
43.	1SB15	STYRENE(1):BENZENE(1)	2.7	2.30	50	43.71	0.125
44.	1ST15	STYRENE(1):TOLUENE(1)	2.4	2.38	50	34.66	0.099
45.	2SA16	STYRENE(1):ACETONE(2)	5.1	20.60	50	56.29	0.162
46.	2SC16	STYRENE(1):CHLOROFORM(2)	4.1	4.81	50	53.20	0.153
47.	3SA17	STYRENE(1):ACETONE(3)	5.1	20.60	50	34.66	0.099
48.	3SC17	STYRENE(1):CHLOROFORM(3)	4.1	4.81	50	29.80	0.086
49.	4SA18	STYRENE(1):ACETONE(4)	5.1	20.60	50	22.30	0.064
50.	4SC18	STYRENE(1):CHLOROFORM(4)	4.1	4.81	50	23.40	0.067

a =David (1995) , b = Michael and Irene (2003)

Table 45: Results of Solution Polymerization of Styrene in various solvent media using BPO initiator.

S/N	SAMPLES	SOLVENTS	REACTION TIME (mins)	CONVERSION (X%)	$R_{p=\frac{d[p]}{dt}} \left\{ \frac{mol}{L.s} \right\} 10^{-2}$
1.	1SA11	ACETONE	10	81.90	1.176
2.	1SC11	CHLOROFORM	10	49.90	0.716
3.	1SB11	BENZENE	10	19.87	0.285
4.	1ST11	TOLUENE	10	09.71	0.139
5.	SE1	ETHYLACETATE	10	65.57	0.941
6.	1SA12	ACETONE	20	86.47	0.620
7.	1SC12	CHLOROFORM	20	73.07	0.524
8.	1SB12	BENZENE	20	30.68	0.220
9.	1ST12	TOLUENE	20	12.36	0.089

10.	SE2	ETHYLACETATE	20	76.35	0.548
11.	SD2	DIMETHYLSULFOXIDE	20	66.22	0.475
12.	SACN2	ACETONITRILE	20	63.81	0.458
13.	1SA13	ACETONE	30	88.81	0.425
14.	1SC13	CHLOROFORM	30	78.37	0.375
15.	1SB13	BENZENE	30	51.21	0.245
16.	1ST13	TOLUENE	30	18.98	0.091
17.	SE3	ETHYLACETATE	30	76.56	0.366
18.	SD3	DIMETHYLSULFOXIDE	30	75.24	0.360
19.	SACN3	ACETONITRILE	30	65.35	0.313
20.	1SA14	ACETONE	40	84.40	0.303
21.	1SC14	CHLOROFORM	40	79.03	0.284
22.	1SB14	BENZENE	40	51.88	0.176
23.	1ST14	TOLUENE	40	20.09	0.072
24.	SE4	ETHYLACETATE	40	79.21	0.284
25.	SD4	DIMETHYLSULFOXIDE	40	86.91	0.312
26.	SACN4	ACETONITRILE	40	69.31	0.249
27.	1SA15	ACETONE	50	84.85	0.244
28.	1SC15	CHLOROFORM	50	78.59	0.226
29.	1SB15	BENZENE	50	50.55	0.145
30.	1ST15	TOLUENE	50	20.53	0.059
31.	SE5	ETHYLACETATE	50	80.53	0.231
32.	SD5	DIMETHYLSULFOXIDE	50	86.69	0.249
33.	SACN5	ACETONITRILE	50	73.92	0.212
34.	SD6	DIMETHYLSULFOXIDE	60	91.60	0.219
35.	SACN	ACETONITRILE	60	82.29	0.197

Table 46: Results of Solution Polymerization of Styrene in solvent media using BPO BLEND as initiator.

S/N	SAMPLES	SOLVENTS	REACTION TIME (mins)	CONVERSION (X%)	$R_{p=\frac{d[p]}{dt}} \left\{ \frac{mol}{L.s} \right\} 10^{-2}$
1.	1SA11	ACETONE	10	82.78	1.188
2.	1SC11	CHLOROFORM	10	49.67	0.713
3.	1SB11	BENZENE	10	39.07	0.561
4.	1ST11	TOLUENE	10	15.23	0.219
5.	SE1	ETHYLACETATE	10	64.03	0.919
6.	1SA12	ACETONE	20	87.92	0.631
7.	1SC12	CHLOROFORM	20	81.68	0.586
8.	1SB12	BENZENE	20	41.06	0.295
9.	1ST12	TOLUENE	20	35.76	0.257
10.	SE2	ETHYLACETATE	20	74.59	0.535
11.	SD2	DIMETHYLSULFOXIDE	20	64.91	0.466

12.	SACN2	ACETONITRILE	20	66.23	0.475
13.	1SA13	ACETONE	30	83.82	0.401
14.	1SC13	CHLOROFORM	30	73.51	0.352
15.	1SB13	BENZENE	30	39.29	0.188
16.	1ST13	TOLUENE	30	36.42	0.174
17.	SE3	ETHYLACETATE	30	74.37	0.356
18.	SD3	DIMETHYLSULFOXIDE	30	73.92	0.354
19.	SACN3	ACETONITRILE	30	68.43	0.327
20.	1SA14	ACETONE	40	85.48	0.307
21.	1SC14	CHLOROFORM	40	84.77	0.304
22.	1SB14	BENZENE	40	42.38	0.152
23.	1ST14	TOLUENE	40	38.19	0.137
24.	SE4	ETHYLACETATE	40	79.87	0.287
25.	SD4	DIMETHYLSULFOXIDE	40	75.47	0.271
26.	SACN4	ACETONITRILE	40	71.07	0.255
27.	1SA15	ACETONE	50	85.40	0.245
28.	1SC15	CHLOROFORM	50	85.65	0.246
29.	1SB15	BENZENE	50	43.71	0.125
30.	1ST15	TOLUENE	50	34.66	0.099
31.	SE5	ETHYLACETATE	50	80.75	0.232
32.	SD5	DIMETHYLSULFOXIDE	50	87.13	0.250
33.	SACN5	ACETONITRILE	50	74.81	0.215
34.	SD6	DIMETHYLSULFOXIDE	60	80.43	0.216
35.	SACN6	ACETONITRILE	60	79.87	0.191

APPENDIX B

Algorithm for the Estimation of Live and Dead Moments using Maple Software.

```
sol[3] = (0.8741913089, 0.5891074777 + 0.4819876398 I, restart;

SOL := proc (tim, C1, T) local B, C, D, R, k, f, beta, E; B := 2.57+(-1)*5.05*T/10^3; C := 9.56+(-1)*1.76*T/10^2; D := -3.03+(-1)*7.85*T/10^3; R := 1.987; k[p] := evalf(6.128*10^8*exp((-1)*7067.8/((R*T)))); k[d] := evalf(7.409*10^16*exp((-1)*31360.7/((R*T)))); k[t] := evalf(7.53*10^10*exp(-1680/(R*T))); f := .7; k[beta] := 2*k[p]*(f*k[d]/k[t])^(1/2)*C1^(1/2)/k[d]; E := 1/(1-x)+2*B*x+2*C*x^2+2*D*x^3 = (1/2)*k[beta]*k[d]*tim-1/ln(k[beta]); return solve(E) end proc;

C := [0.825e-1, 0.620e-1, 0.413e-1, 0.206e-1];

[0.0825, 0.0620, 0.0413, 0.0206]

for i to nops(C) do sol[i] = SOL(10, C[i], 393) end do;

sol[1] = (0.8477374396, 0.5759056178 + 0.4034509157 I,
-0.5673036404, 0.5759056178 - 0.4034509157 I)

sol[2] = (0.7842372058, 0.5729688095 + 0.2657697484 I,
-0.4979297899, 0.5729688095 - 0.2657697484 I)

sol[3] = (0.3747133565, 0.7432998063 + 0.1600267640 I,
-0.4290679343, 0.7432998063 - 0.1600267640 I)

sol[4] = (0.1549280070, 0.8091549464 + 0.1890248796 I,
-0.3409928649, 0.8091549464 - 0.1890248796 I)

for i to nops(C) do sol[i] = SOL(10, C[i], 363) end do;

sol[1] = (0.9727476441 + 0.2280573763 I,
-0.2030671413 + 0.4058136419 I, -0.2030671413 - 0.4058136419 I,
0.9727476441 - 0.2280573763 I)

sol[2] = (0.9836731298 + 0.2253663256 I,
-0.2139926271 + 0.4379912395 I, -0.2139926271 - 0.4379912395 I,
0.9836731298 - 0.2253663256 I)

sol[3] = (1.012449703 + 0.2163466007 I,
```

-0.2427692003 + 0.5161453963 I, -0.2427692003 - 0.5161453963 I,
1.012449703 - 0.2163466007 I)

sol[4] = (0.9711028046, 0.9074622606 + 1.140752899 I,
-1.246666320, 0.9074622606 - 1.140752899 I)

for i to nops(C) do sol[i] = SOL(10, C[i], 333) end do;

sol[1] = (1.000455343 + 0.2451713198 I,
-0.1727474031 + 0.3137877521 I, -0.1727474031 - 0.3137877521 I,
1.000455343 - 0.2451713198 I)

sol[2] = (1.001697569 + 0.2446614692 I,
-0.1739896285 + 0.3187951467 I, -0.1739896285 - 0.3187951467 I,
1.001697569 - 0.2446614692 I)

sol[3] = (1.003840969 + 0.2437720123 I,
-0.1761330283 + 0.3272826149 I, -0.1761330283 - 0.3272826149 I,
1.003840969 - 0.2437720123 I)

sol[4] = (1.009132185 + 0.2415218365 I,
-0.1814242447 + 0.3474894184 I, -0.1814242447 - 0.3474894184 I,
1.009132185 - 0.2415218365 I)

NULL;

for i to nops(C) do sol[i] = SOL(20, C[i], 393) end do;

sol[1] = (0.8746813622, 0.5894483327 + 0.4836007555 I,
-0.6213329928, 0.5894483327 - 0.4836007555 I)

sol[2] = (0.8408123873, 0.5738943284 + 0.3853085870 I,
-0.5563560093, 0.5738943284 - 0.3853085870 I)

sol[3] = (0.7719422587, 0.5754454258 + 0.2455248673 I,

-0.4905880754, 0.5754454258 - 0.2455248673 I)
 sol[4] = (0.2994518555, 0.7692725812 + 0.1726053711 I,
 -0.4057519830, 0.7692725812 - 0.1726053711 I)
 for i to nops(C) do sol[i] = SOL(20, C[i], 363) end do;
 sol[1] = (0.9702593636 + 0.2286187309 I,
 -0.2005788609 + 0.3982326253 I, -0.2005788609 - 0.3982326253 I,
 0.9702593636 - 0.2286187309 I)
 sol[2] = (0.9816439903 + 0.2258946649 I,
 -0.2119634876 + 0.4321408105 I, -0.2119634876 - 0.4321408105 I,
 0.9816439903 - 0.2258946649 I)
 sol[3] = (1.011025875 + 0.2168644244 I,
 -0.2413453723 + 0.5124562088 I, -0.2413453723 - 0.5124562088 I,
 1.011025875 - 0.2168644244 I)
 sol[4] = (0.9711426401, 0.9077828656 + 1.141396998 I,
 -1.247347366, 0.9077828656 - 1.141396998 I)
 for i to nops(C) do sol[i] = SOL(20, C[i], 333) end do;
 sol[1] = (1.000291654 + 0.2452381985 I,
 -0.1725837142 + 0.3131228650 I, -0.1725837142 - 0.3131228650 I,
 1.000291654 - 0.2452381985 I)
 sol[2] = (1.001556629 + 0.2447195220 I,
 -0.1738486888 + 0.3182303779 I, -0.1738486888 - 0.3182303779 I,
 1.001556629 - 0.2447195220 I)
 sol[3] = (1.003727271 + 0.2438195070 I,
 -0.1760193312 + 0.3268370521 I, -0.1760193312 - 0.3268370521 I,

1.003727271 - 0.2438195070 I)

sol[4] = (1.009054138 + 0.2415556055 I,
-0.1813461973 + 0.3471984380 I, -0.1813461973 - 0.3471984380 I,
1.009054138 - 0.2415556055 I)

NULL;

for i to nops(C) do sol[i] = SOL(30, C[i], 393) end do;

sol[1] = (0.8918489429, 0.6041425587 + 0.5445940158 I,
-0.6678890255, 0.6041425587 - 0.5445940158 I)

sol[2] = (0.8676354617, 0.5849166908 + 0.4610101720 I,
-0.6052238084, 0.5849166908 - 0.4610101720 I)

sol[3] = (0.8292815739, 0.5716362566 + 0.3569988481 I,
-0.5403090524, 0.5716362566 - 0.3569988481 I)

sol[4] = (0.5193643534, 0.6839464660 + 0.1304981816 I,
-0.4550122506, 0.6839464660 - 0.1304981816 I)

for i to nops(C) do sol[i] = SOL(30, C[i], 363) end do;

sol[1] = (0.9677360114 + 0.2291691170 I,
-0.1980555086 + 0.3904370935 I, -0.1980555086 - 0.3904370935 I,
0.9677360114 - 0.2291691170 I)

sol[2] = (0.9795923119 + 0.2264154442 I,
-0.2099118091 + 0.4261698576 I, -0.2099118091 - 0.4261698576 I,
0.9795923119 - 0.2264154442 I)

sol[3] = (1.009591809 + 0.2173779984 I,
-0.2399113066 + 0.5087243834 I, -0.2399113066 - 0.5087243834 I,
1.009591809 - 0.2173779984 I)

```

sol[4] = (0.9711823642, 0.9081031878 + 1.142040385 I,
-1.248027734, 0.9081031878 - 1.142040385 I)
for i to nops(C) do sol[i] = SOL(30, C[i], 333) end do;
sol[1] = (1.000127820 + 0.2453050661 I,
-0.1724198796 + 0.3124561819 I, -0.1724198796 - 0.3124561819 I,
1.000127820 - 0.2453050661 I)
sol[2] = (1.001415582 + 0.2447775661 I,
-0.1737076413 + 0.3176643276 I, -0.1737076413 - 0.3176643276 I,
1.001415582 - 0.2447775661 I)
sol[3] = (1.003613505 + 0.2438669954 I,
-0.1759055644 + 0.3263907060 I, -0.1759055644 - 0.3263907060 I,
1.003613505 - 0.2438669954 I)
sol[4] = (1.008976058 + 0.2415893710 I,
-0.1812681175 + 0.3469071366 I, -0.1812681175 - 0.3469071366 I,
1.008976058 - 0.2415893710 I)
NULL;
for i to nops(C) do sol[i] = SOL(40, C[i], 393) end do;
sol[1] = (0.9041699627, 0.6186165538 + 0.5947772089 I,
-0.7091580355, 0.6186165538 - 0.5947772089 I)
sol[2] = (0.8849261758, 0.5975347966 + 0.5188880183 I,
-0.6477507342, 0.5975347966 - 0.5188880183 I)
sol[3] = (0.8565082807, 0.5792450249 + 0.4277709498 I,
-0.5827532958, 0.5792450249 - 0.4277709498 I)
sol[4] = (0.7809852082, 0.5735529294 + 0.2602360883 I,
-0.4958460322, 0.5735529294 - 0.2602360883 I)

```



```

for i to nops(C) do sol[i] = SOL(40, C[i], 363) end do;

sol[1] = (0.9651763262 + 0.2297083093 I,
-0.1954958235 + 0.3824116711 I, -0.1954958235 - 0.3824116711 I,
0.9651763262 - 0.2297083093 I)

sol[2] = (0.9775174580 + 0.2269285502 I,
-0.2078369552 + 0.4200721956 I, -0.2078369552 - 0.4200721956 I,
0.9775174580 - 0.2269285502 I)

sol[3] = (1.008147320 + 0.2178872965 I,
-0.2384668171 + 0.5049487136 I, -0.2384668171 - 0.5049487136 I,
1.008147320 - 0.2178872965 I)

sol[4] = (0.9712219774, 0.9084232278 + 1.142683062 I,
-1.248707428, 0.9084232278 - 1.142683062 I)

for i to nops(C) do sol[i] = SOL(40, C[i], 333) end do;

sol[1] = (0.9999638390 + 0.2453719227 I,
-0.1722558988 + 0.3117876903 I, -0.1722558988 - 0.3117876903 I,
0.9999638390 - 0.2453719227 I)

sol[2] = (1.001274426 + 0.2448356015 I,
-0.1735664860 + 0.3170969884 I, -0.1735664860 - 0.3170969884 I,
1.001274426 - 0.2448356015 I)

sol[3] = (1.003499668 + 0.2439144777 I,
-0.1757917277 + 0.3259435731 I, -0.1757917277 - 0.3259435731 I,
1.003499668 - 0.2439144777 I)

sol[4] = (1.008897945 + 0.2416231329 I,
-0.1811900052 + 0.3466155132 I, -0.1811900052 - 0.3466155132 I,
1.008897945 - 0.2416231329 I)

```

NULL;

for i to nops(C) do sol[i] = SOL(50, C[i], 393) end do;

sol[1] = (0.9136077846, 0.6325424003 + 0.6378877020 I,

-0.7464475505, 0.6325424003 - 0.6378877020 I)

sol[2] = (0.8974431970, 0.6102495298 + 0.5666182505 I,

-0.6856972219, 0.6102495298 - 0.5666182505 I)

- 0.3398238885 I)

for i to nops(C) do sol[i] = SOL(-0.6201612294, 0.5891074777 - 0.4819876398 I)

sol[4] = (0.8218071738, 0.5708264263 + 0.3398238885 I,

-0.5312149915, 0.5708264263 50, C[i], 363) end do;

sol[1] = (0.9625789729 + 0.2302360698 I,

-0.1928984702 + 0.3741391279 I, -0.1928984702 - 0.3741391279 I,

0.9625789729 - 0.2302360698 I)

sol[2] = (0.9754187631 + 0.2274338639 I,

-0.2057382603 + 0.4138411152 I, -0.2057382603 - 0.4138411152 I,

0.9754187631 - 0.2274338639 I)

sol[3] = (1.006692215 + 0.2183922913 I,

-0.2370117121 + 0.5011279378 I, -0.2370117121 - 0.5011279378 I,

1.006692215 - 0.2183922913 I)

sol[4] = (0.9712614802, 0.9087429863 + 1.143325032 I,

-1.249386447, 0.9087429863 - 1.143325032 I)

for i to nops(C) do sol[i] = SOL(50, C[i], 333) end do;

sol[1] = (0.9997997118 + 0.2454387683 I,

-0.1720917716 + 0.3111173779 I, -0.1720917716 - 0.3111173779 I,

0.9997997118 - 0.2454387683 I)

sol[2] = (1.001133163 + 0.2448936283 I,
-0.1734252225 + 0.3165283530 I, -0.1734252225 - 0.3165283530 I,
1.001133163 - 0.2448936283 I)

sol[3] = (1.003385761 + 0.2439619537 I,
-0.1756778211 + 0.3254956500 I, -0.1756778211 - 0.3254956500 I,
1.003385761 - 0.2439619537 I)

sol[4] = (1.008819801 + 0.2416568912 I,
-0.1811118604 + 0.3463235671 I, -0.1811118604 - 0.3463235671 I,
1.008819801 - 0.2416568912 I)

NULL;

sol = SOL(50, 0.825e-1, 363);

sol = (0.9625789729 + 0.2302360698 I,
-0.1928984702 + 0.3741391279 I, -0.1928984702 - 0.3741391279 I,
0.9625789729 - 0.2302360698 I)

NULL;

sol = SOL(30, 0.825e-1, 363);

sol = (0.9677360114 + 0.2291691170 I,
-0.1980555086 + 0.3904370935 I, -0.1980555086 - 0.3904370935 I,
0.9677360114 - 0.2291691170 I)

NULL;

sol = SOL(30, 0.5155e-1, 333);

sol = (1.002352869 + 0.2443908533 I,
-0.1746449286 + 0.3214100273 I, -0.1746449286 - 0.3214100273 I,

1.002352869 - 0.2443908533 I)

NULL;

sol = SOL(50, 0.825e-1, 393);

sol = (0.9136077846, 0.6325424003 + 0.6378877020 I,
-0.7464475505, 0.6325424003 - 0.6378877020 I)

NULL;

sol = SOL(30, .11345, 333);

sol = (0.9988770383 + 0.2458132453 I,
-0.1711690981 + 0.3073259125 I, -0.1711690981 - 0.3073259125 I,
0.9988770383 - 0.2458132453 I)

NULL;

sol = SOL(50, .11345, 363);

sol = (0.9518361825 + 0.2322185712 I,
-0.1821556797 + 0.3383311706 I, -0.1821556797 - 0.3383311706 I,
0.9518361825 - 0.2322185712 I)

NULL;

sol = SOL(30, 0.825e-1, 393);

sol = (0.8918489429, 0.6041425587 + 0.5445940158 I,
-0.6678890255, 0.6041425587 - 0.5445940158 I)

NULL;

sol = SOL(70, .11345, 333);

sol = (0.9981013049 + 0.2461263768 I,
-0.1703933647 + 0.3041070379 I, -0.1703933647 - 0.3041070379 I,
0.9981013049 - 0.2461263768 I)

NULL;

sol = SOL(30, 0.5155e-1, 393);

sol = (0.8513566979, 0.5771713946 + 0.4132979603 I,
-0.5734544523, 0.5771713946 - 0.4132979603 I)

NULL;

sol = SOL(70, 0.5155e-1, 393);

sol = (0.9069243678, 0.6223989644 + 0.6068932423 I,
-0.7194772617, 0.6223989644 - 0.6068932423 I)

NULL;

sol = SOL(50, 0.825e-1, 363);

sol = (0.9625789729 + 0.2302360698 I,
-0.1928984702 + 0.3741391279 I, -0.1928984702 - 0.3741391279 I,
0.9625789729 - 0.2302360698 I)

NULL;

sol = SOL(70, .11345, 393);

sol = (0.9441129026, 0.7037715398 + 0.8212712580 I,
-0.9194109475, 0.7037715398 - 0.8212712580 I)

NULL;

sol = SOL(30, 0.5155e-1, 363);

sol = (0.9903703504 + 0.2235266311 I,
-0.2206898476 + 0.4569397343 I, -0.2206898476 - 0.4569397343 I,
0.9903703504 - 0.2235266311 I)

NULL;

sol = SOL(70, 0.825e-1, 363);

sol = (0.9572655154 + 0.2312562777 I,

-0.1875850126 + 0.3567724397 I, -0.1875850126 - 0.3567724397 I,
0.9572655154 - 0.2312562777 I)

APPENDIX C

Data obtained from the Response Surface Methodology Tool

%c	PREDICTED	RESIDUAL
47.46	48.2265	-0.76652
48.12	48.2265	-0.10652
33.55	37.5324	-3.98239
48.34	50.5331	-2.19311
48.79	48.2265	0.56348
45.92	48.4356	-2.51559
57.84	58.4023	-0.56230
44.37	45.1575	-0.78745
76.82	76.4140	0.40601
45.25	40.5936	4.65641
34.88	36.0242	-1.14425
54.31	52.5327	1.77735
49.00	48.2265	0.77348
55.19	55.1408	0.04921
75.28	72.0359	3.24415
47.24	48.2265	-0.98652
48.57	48.2265	0.34348
58.72	55.4829	3.23714
34.44	32.8337	1.60633
74.39	78.0024	-3.61238

Factors:	3	Replicates:	1
Base runs:	20	Total runs:	20
Base blocks:	1	Total blocks:	1

Two-level factorial: Full factorial

Cube points: 8
 Center points in cube: 6
 Axial points: 6
 Center points in axial: 0

Alpha: 1.68179

Design Table (randomized)

Run	Blk	A	B	C
1	1	0.00000	0.00000	0.00000
2	1	0.00000	0.00000	0.00000
3	1	-1.00000	-1.00000	-1.00000
4	1	1.68179	0.00000	0.00000
5	1	0.00000	0.00000	0.00000
6	1	-1.00000	-1.00000	1.00000
7	1	0.00000	0.00000	1.68179
8	1	1.00000	-1.00000	1.00000
9	1	-1.00000	1.00000	1.00000
10	1	0.00000	-1.68179	0.00000
11	1	1.00000	-1.00000	-1.00000
12	1	1.00000	1.00000	-1.00000
13	1	0.00000	0.00000	0.00000
14	1	-1.00000	1.00000	-1.00000
15	1	1.00000	1.00000	1.00000
16	1	0.00000	0.00000	0.00000
17	1	0.00000	0.00000	0.00000
18	1	-1.68179	0.00000	0.00000
19	1	0.00000	0.00000	-1.68179
20	1	0.00000	1.68179	0.00000

Central Composite Design

Factors: 3 Replicates: 1
 Base runs: 20 Total runs: 20
 Base blocks: 1 Total blocks: 1

Two-level factorial: Full factorial

Cube points: 8
 Center points in cube: 6
 Axial points: 6
 Center points in axial: 0

Alpha: 1.68179

Design Table (randomized)

Run	Blk	A	B	C
1	1	0.00000	0.00000	0.00000
2	1	0.00000	0.00000	0.00000
3	1	-1.00000	-1.00000	-1.00000
4	1	1.68179	0.00000	0.00000
5	1	0.00000	0.00000	0.00000
6	1	-1.00000	-1.00000	1.00000
7	1	0.00000	0.00000	1.68179
8	1	1.00000	-1.00000	1.00000
9	1	-1.00000	1.00000	1.00000
10	1	0.00000	-1.68179	0.00000
11	1	1.00000	-1.00000	-1.00000
12	1	1.00000	1.00000	-1.00000

13	1	0.00000	0.00000	0.00000
14	1	-1.00000	1.00000	-1.00000
15	1	1.00000	1.00000	1.00000
16	1	0.00000	0.00000	0.00000
17	1	0.00000	0.00000	0.00000
18	1	-1.68179	0.00000	0.00000
19	1	0.00000	0.00000	-1.68179
20	1	0.00000	1.68179	0.00000

Results for: Worksheet 3

Response Surface Regression: %c versus REACTION TIM, REACTION TEM, INITIATOR CO

The analysis was done using coded units.

Estimated Regression Coefficients for %c

Term	Coef	SE Coef	T	P
Constant	48.2265	1.2470	38.673	0.000
REACTION TIME	-1.4716	0.8274	-1.779	0.106
REACTION TEMPERATURE	11.1217	0.8274	13.442	0.000
INITIATOR CONCENTRATION	7.6016	0.8274	9.187	0.000
REACTION TIME*REACTION TIME	1.6905	0.8054	2.099	0.062
REACTION TEMPERATURE*	3.9144	0.8054	4.860	0.001
REACTION TEMPERATURE				
INITIATOR CONCENTRATION*	-0.9223	0.8054	-1.145	0.279
INITIATOR CONCENTRATION				
REACTION TIME*REACTION TEMPERATURE	-0.2750	1.0810	-0.254	0.804
REACTION TIME*	-0.4425	1.0810	-0.409	0.691
INITIATOR CONCENTRATION				
REACTION TEMPERATURE*	2.5925	1.0810	2.398	0.037
INITIATOR CONCENTRATION				

S = 3.05762 PRESS = 695.052
R-Sq = 96.81% R-Sq(pred) = 76.30% R-Sq(adj) = 93.94%

Analysis of Variance for %c

Source	DF	Seq SS	Adj SS
Regression	9	2839.34	2839.34
Linear	3	2507.97	2507.97
REACTION TIME	1	29.57	29.57
REACTION TEMPERATURE	1	1689.25	1689.25
INITIATOR CONCENTRATION	1	789.15	789.15
Square	3	275.42	275.42
REACTION TIME*REACTION TIME	1	29.60	41.18
REACTION TEMPERATURE*REACTION TEMPERATURE	1	233.57	220.81
INITIATOR CONCENTRATION*INITIATOR CONCENTRATION	1	12.26	12.26
Interaction	3	55.94	55.94
REACTION TIME*REACTION TEMPERATURE	1	0.60	0.60
REACTION TIME*INITIATOR CONCENTRATION	1	1.57	1.57
REACTION TEMPERATURE*INITIATOR CONCENTRATION	1	53.77	53.77
Residual Error	10	93.49	93.49
Lack-of-Fit	5	90.89	90.89
Pure Error	5	2.60	2.60
Total	19	2932.83	

Source	Adj MS	F	P
Regression	315.48	33.74	0.000

Linear	835.99	89.42	0.000
REACTION TIME	29.57	3.16	0.106
REACTION TEMPERATURE	1689.25	180.69	0.000
INITIATOR CONCENTRATION	789.15	84.41	0.000
Square	91.81	9.82	0.003
REACTION TIME*REACTION TIME	41.18	4.41	0.062
REACTION TEMPERATURE*REACTION TEMPERATURE	220.81	23.62	0.001
INITIATOR CONCENTRATION*INITIATOR CONCENTRATION	12.26	1.31	0.279
Interaction	18.65	1.99	0.179
REACTION TIME*REACTION TEMPERATURE	0.60	0.06	0.804
REACTION TIME*INITIATOR CONCENTRATION	1.57	0.17	0.691
REACTION TEMPERATURE*INITIATOR CONCENTRATION	53.77	5.75	0.037
Residual Error	9.35		
Lack-of-Fit	18.18	34.95	0.001
Pure Error	0.52		
Total			

Estimated Regression Coefficients for %c using data in uncoded units

Term	Coef
Constant	53.2398
REACTION TIME	-0.395978
REACTION TEMPERATURE	-0.619582
INITIATOR CONCENTRATION	188.920
REACTION TIME*REACTION TIME	0.00422626
REACTION TEMPERATURE*	0.00434928
REACTION TEMPERATURE	
INITIATOR CONCENTRATION*	-962.788
INITIATOR CONCENTRATION	
REACTION TIME*REACTION TEMPERATURE	-4.58333E-04
REACTION TIME*	-0.714863
INITIATOR CONCENTRATION	
REACTION TEMPERATURE*	2.79214
INITIATOR CONCENTRATION	

Residual Plots for %c

Contour Plots of %c

Surface Plots of %c

Results for: Worksheet 4

Optimal Design: REACTION TIME, REACTION TEMPERATURE, INITIATOR CONCENTRATION

Data Matrix

Run	A	B	C
5	50.000	140.454	0.082
9	83.636	90.000	0.082
4	70.000	120.000	0.052
11	30.000	60.000	0.113
2	30.000	120.000	0.052

7	70.000	60.000	0.052
1	70.000	60.000	0.113
10	50.000	90.000	0.135
8	30.000	60.000	0.052
6	30.000	120.000	0.113
3	50.000	90.000	0.082

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Results for: Worksheet 3

Contour Plot of %c vs REACTION TEMPERATURE, REACTION TIME

Contour Plot of %c vs INITIATOR CONCENTRATION, REACTION TIME

Contour Plot of %c vs INITIATOR CONCENTRATION, REACTION TEMPERATURE

Surface Plot of %c vs REACTION TEMPERATURE, REACTION TIME

Surface Plot of %c vs INITIATOR CONCENTRATION, REACTION TIME

Surface Plot of %c vs INITIATOR CONCENTRATION, REACTION TEMPERATURE