



**Ain Shams University**  
**Faculty of Women's for Arts, Science and Education**  
**Chemistry Department**

# **Synthesis and Evaluation of Some Hydrophobically Modified Polyacrylamide Nanolatexes Using Novel Polymerizable Surfactants for Enhanced Oil Recovery**

A Thesis  
Submitted for  
Ph.D. Degree of Science  
In  
Organic Chemistry

Presented by

**El-Sayed Abd Al-Rahman El-Sayed El-Sharaky**  
**(MSc. Organic Chemistry, 2006)**

Supervised by

**Prof. Dr. Nadia G. Kandile**  
Prof. of Organic Chemistry  
Faculty of Women  
Ain Shams University

**Prof. Dr. Ahmed M. Al Sabagh**  
Prof. of Applied Chemistry  
Egyptian Petroleum Research Institute

**Dr. Rasha Abd El-Azim El-Ghazawy**  
Ass. Prof of Polymer Chemistry  
Egyptian Petroleum Research Institute

**2013**



Ain Shams University  
Faculty of Women's for Arts, Science and Education  
Chemistry Department

# **Synthesis and Evaluation of Some Hydrophobically Modified Polyacrylamide Nanolatexes Using Novel Polymerizable Surfactants for Enhanced Oil Recovery**

**By**

**El-Sayed Abd Al-Rahman El-Sayed El-Sharaky**

**Thesis Supervisors**

Prof. Dr. Nadia G. Kandile  
Prof. Dr. Ahmed M. Al Sabagh  
Prof. Dr. Rasha El-Ghazawy

**Thesis approved**

.....  
.....  
.....

**Head of Chemistry Department  
Prof. Dr. Fateen Zakaria**



جامعة عين شمس  
كلية البنات للعلوم والآداب والتربية  
قسم الكيمياء

## تخليق و تقييم بعض بوليمرات الأكريل أميد المعدلة المتناهية الصغر باستخدام مواد ذات نشاط سطحي مبتكرة قابلة للبلمرية و ذلك لتطبيقها فى مجال رفع الحصيللة البترولية

رسالة مقدمه من

السيد عبد الرحمن السيد الشراقى  
ماجستير فى العلوم - كيمياء عضوية 2008 م

للحصول علي  
درجة دكتوراه الفلسفه فى العلوم  
(كيمياء عضوية)

تحت إشراف

أ.د/ أحمد محمد أحمد الصباغ  
الأستاذ الكيمياء التطبيقية  
معهد بحوث البترول

أ.د/ نادية غريب قنـديل  
أستاذ الكيمياء العضوية  
كلية البنات - جامعة عين شمس

د/ رشا عبدالعظيم الغزاوى  
أستاذ مساعد كيمياء البلمرات  
معهد بحوث البترول

2013



جامعة عين شمس  
كلية البنات للاداب والعلوم والتربية  
قسم الكيمياء  
رسالة دكتوراة

اسم الطالب: السيد عبد الرحمن السيد الشراقي

عنوان الرسالة

" تخليق و تقييم بعض بوليمرات الأكريل أميد المعدلة المتناهية الصغر  
باستخدام مواد ذات نشاط سطحي مبتكرة قابلة للبلمرة و ذلك لتطبيقها في  
مجال رفع الحصىلة البترولية "

لجنةالأشـــــراف

أ.د/ نادية غريب قنـديل	أستاذ الكيمياء العضوية - كلية البنات - جامعة عين شمس
أ.د/ أحمد محمد أحمد الصباغ	أستاذ الكيمياء التطبيقية - معهد بحوث البترول
د/ رشا عبدالعظيم الغزاوي	أستاذ مساعد كيمياء الهلمرات - معهد بحوث البترول

لجنة الحكم والمناقشة

أ.د/ عبد الرحمن ناصر مختار	أستاذ كيمياء البلمرات - كلية العلوم - جامعة الأزهر
أ.د/ محمود أحمد عبد الغفار	أستاذ كيمياء البلمرات - المركز القومي للبحوث
أ.د/ أحمد محمد أحمد الصباغ	أستاذ الكيمياء التطبيقية - معهد بحوث البترول
أ.د/ نادية غريب قنـديل	أستاذ الكيمياء العضوية - كلية البنات - جامعة عين شمس

تاريخ البحث

2013/ /

تاريخ المنح

2013/ /

الدراسات العليا

ختم الإجازة

موافقة مجلس الكلية

2013 / /

موافقة مجلس الكلية

2013 / /



# Acknowledgment

## ACKNOWLEDGEMENT

I am in a greatest thankful to **ALLAH**, The Most Merciful, The Most Gracious, by the grace of whom the progress and success of the present work.

It is my pleasure to express my deepest thanks to **Prof. Dr. Nadia Gharib Kandile**, Professor of Organic Chemistry, Chemistry Department, Faculty of Arts, Science and Education Ain Shams University, for her kind supervision, valuable discussions, encouragement, careful revision of the manuscript and help given throughout this work.

It is my pleasure to express my deep thanks, appreciation and gratitude to **Prof. Dr. Ahmed M. Al-Sabagh**, Professor of Applied Chemistry, Director of Petroleum Research Institute (EPRI), for suggesting the topic of investigation, direct supervision, careful revision of the manuscript and his kind help given throughout this work.

My deep thanks and appreciation to **Dr. Rasha Abd El-Azim El-Gazawy**, Associate Professor of Polymer Chemistry, Petroleum Research Institute (EPRI), for her support, kind help, co-operation and valuable discussion.

My special thanks and gratitude to **Dr. Mahmoud Reyad Noor El-Din**, Associate Professor of Applied Chemistry, Petroleum Research Institute, for his kind help, encouragement and valuable discussion.

My deep thanks to all my professors, doctors and colleagues in the Egyptian Petroleum Research Institute, Petroleum Applications Department and Special Uses Lab. for support and help.

My deep thanks to my family **My Father**, **My Mother** and **My sisters** for supporting me in my life, and I would like to express my special thanks to **My Wife** for supporting me.

***El-Sayed Abd Al-Rahman El-Sayed El-Sharaky***

## CONTENTS

<b>List of Abbreviations</b>	<b>I</b>
<b>List of Tables</b>	<b>II</b>
<b>List of Figures</b>	<b>III</b>
<b>Aim of the Work</b>	<b>IX</b>
<b>Summary</b>	<b>X</b>
<b>Chapter I: Introduction</b>	<b>1</b>
I.1- Hydrophobically Modified Polymers	
(HM-Ps)	1
I.1.1- Classification of HM-Ps	2
I.1.1.1- Classification According to Localization of Hydrophobic Groups	2
I.1.1.2- Classification According to Chemical Nature of Polymer Backbone	4
I.1.1.3- Classification According to Synthetic Route	5
I.1.3.2- Properties of HM-Ps	7
I.1.3- Hydrophobically Modified Polyacrylamides (HM-PAMs)	13
I.2- Polymerizable Surfactants (Surfmers)	15
I.2.1- Benefits of Strong Attachment	15
I.2.2- Classification of Surfmers	16
I.2.2.1- Regarding The Position of The Polymerizable Group	16
I.2.2.2- Depending on The Nature of The Hydrophilic Moiety	17
I.3- Enhanced Oil Recovery(EOR)	20
I.3.1- Thermal Flooding Processes	22

I.3.2-	Miscible Flooding Processes	23
I.3.3-	Microbial Flooding Processes	24
I.3.4-	Chemical Flooding Processes	25
I.3.4.1-	Polymer Flooding	25
I.3-	Literature Survey	32
<b>Chapter II</b>	<b>Experimental</b>	<b>48</b>
II.1-	Chemicals	48
II.2-	Instruments	49
II.2.1-	Mass Spectrometry (MS)	49
II.2.2-	FT-IR	49
II.2.3-	Proton and Carbon Nuclear Magnetic Resonance ( $^1\text{H}$ and $^{13}\text{C}$ NMR)	49
II.2.4-	Elemental Analysis	49
II.2.5-	Tensiometer	49
II.2.6-	Thermal Gravimetric Analysis (TGA)	49
II.2.7-	Kinematic Viscosity	50
II.2.8-	Gel Permeation Chromatography (GPC)	50
II.2.9-	Dynamic Light Scattering (DLS)	50
II.2.10-	High Resolution Transmission Electron Microscopy (HR-TEM)	50
II.2.11-	Dynamic Viscosity	50
II.3-	Methods of Preparation	51
II.3.1-	Preparation of Polymerizable Surfactants (Surfmers)	51

II.3.1.1- Synthesis of Alkenylsuccinic Anhydrides (ASA)	51
II.3.1.2- Synthesis of Polyoxyethylene Alkenyl succinate Monoesters (Hemiesters (ASA- eo22s))	51
II.3.1.3- Synthesis of Polyoxyethylene Alkenyl succinate Diesters of Aliphatic Fatty Alcohols (A-AS-eo22s)	52
II.3.1.4- Synthesis of Acrylate Esters of Hemi (ASA- eo22Acs) and Diesters (A-AS-eo22Acs) (Surfmers)	52
II.3.2- Preparation of Hydrophobically Modified Polyacrylamides (HM-PAMs) and Polyacrylamide (PAM)	53
II.3.2.1- Preparation of HM-PAMs	53
II. 3.2.2- Preparation of PAM	53
II.4- Measurements	54
II.4.1- Surface Tension and CMC Determination for The Surfmers	54
II.4.2- Acid Value Titration Method	54
II.4.3- Molecular Weight Determination	54
II.4.4- Rheological Measurements	55
II.4.5- Surface and Interfacial Tension for PAM and HM-PAMs	56
II.4.6- Emulsification	56

<b>Chapter III</b>	<b>Results and Discussion</b>	<b>57</b>
III.1-	Polymerizable Surfactants (Surfmers)	57
III.1.1-	Chemical Structure Justification of Polymerizable Surfactants (Surfmers)	57
III.1.1.1-	Preparation of Alkenylsuccinic Anhydrides (ASA)	59
III.1.1.2-	Preparation of Polyoxyethylene Alkenyl succinate Monoesters (Hemiester (ASA- eo22s))	59
III.1.1.3-	Preparation of Polyoxyethylene Alkenyl succinate Diesters of Aliphatic Fatty Alcohols (A-AS-eo22s)	61
III.1.1.4-	Preparation of Acrylate Esters of Hemi (ASA-eo22Acs) and Diesters (A-AS- eo22Acs) (Surfmers)	61
III.1.1.5-	Elemental Analysis of The Prepared Base, Hemiester, Diester and Surfmers	73
III.1.1.6-	Acid Value Titration Method of The Prepared Base and Hemiester	74
III.1.2-	Surface Active Properties and Thermodynamic Parameters of The Prepared Surfmers	75
III.2-	Hydrophobically Modified Polyacrylamides (HM-PAMs) and Their Corresponding Unmodified Polyacrylamide (PAM)	90

III.2.1- Chemical Structure Justification of Hydrophobically Modified Polyacrylamides (HM-PAMs) and Their Corresponding Unmodified Polyacrylamide (PAM)	90
III.2.2- Thermal Gravimetric Analysis of The Prepared Polyacrylamide (PAM) and Copolymers (HM-PAMs)	103
III.2.3- Size of Microemulsion Droplets, Latex Particles and Latex Particles Morphologies	105
III.2.4- Molecular Weights of The Prepared Polymers (PAM) and Copolymers (HM-PAMs)	109
III.2.5- Solution Properties of The Polymer (PAM) and Copolymers (HM-PAMs)	113
III.2.5.1- Critical Association Concentration ( $C^*$ ) and Effect of Concentration on Apparent Viscosity ( $\eta_{app}$ )	113
III.2.5.2- Effect of Added Salts	125
III.2.5.2.1- Effect of Sodium Chloride (Monovalent Cations)	125
III.2.5.2.2- Effect of Calcium Chloride (Divalent Cations)	129
III.2.5.3- Effect of Temperature	132
III.2.5.4- Effect of Shear Rate	136
III.2.5.5- Effect of Aging	140
III.2.5.6- Surface, Interfacial Tension and	142

	Emulsification Efficiency	
	<b>Conclusion</b>	<b>151</b>
<b>Chapter IV</b>	<b>References</b>	<b>153</b>
	<b>Arabic Summary</b>	

## **List of Abbreviations**

<b>Abbreviation</b>	<b>Meaning</b>
HM-Ps	Hydrophobically Modified Polymers
IOR	Improved Oil Recovery
HEUR	Hydrophobically Ethoxylated Urethane
HASE	Hydrophobically Alkali Soluble or Swellable Emulsion
HM-HEC	Hydrophobically Modified Hydroxyethyl Cellulose
HM-PEO	Hydrophobically Modified Polyethylene Oxide
HM-PAA	Hydrophobically Modified Polyacrylic Acid
HM-PAM	Hydrophobically Modified Polyacrylamide
Surfmer	Polymerizable Surfactant
EOR	Enhanced Oil Recovery
LPGs	Liquefied Petroleum Gases
MEOR	Microbial Enhanced Oil Recovery
HPAM	Hydrolyzed Polyacrylamide
HEC	Hydroxyl Ethyl Cellulose
HAP	Hydrophobically Associating Polymer
CMC	Critical Micelle Concentration
ASA	Alkenyl Succinic Anhydride
PAM	Polyacrylamide
CAC	Critical Association Concentration

## **List of Tables**

<b>Table</b>	<b>Page</b>
(1) Characteristics of Different Polymer Structures	27
(2) Chemicals Used Throughout The Investigation	48
(3) The Elemental Composition of OSA, DDSA and ODSA Based Series	73
(4) Acid Values of Alkenylsuccinic Anhydrides and Their Hemiesters	74
(5) Surface Active Properties of The Prepared Surfmers	82
(6) Thermodynamic Parameters of Micellization and Adsorption and Structural Effects on Micellization and Adsorption for The Prepared Surfmers	83
(7) Abbreviations, Yield, Intrinsic Viscosities $[\eta]$ and Molecular Weights of The Prepared HM-PAMs and PAM	112
(8) Effect of Aging on The Apparent Viscosities of HM-PAMs and PAM at 55 °C for 45 Days	141
(9) The Stability of The Crude Oil Emulsions Formed by 0.5 g/dl HM-PAMs and PAM Brine Solutions for 7 Days at 30 °C	150

## **List of Figures**

<b>Figure</b>	<b>Page</b>
(1) Schematic Illustration of The Structure of (a) Telechelic and (b) Comb Like HM-Ps	3
(2) Polymer Concentration Intervals: Dilute Regime ( $c < c^*$ ), Semi Dilute Regime ( $c \sim c^*$ ) and Concentrated Regime ( $c > c^*$ )	8
(3) Schematic illustration of Hydrophobic-Association for HM-Ps, (a) Intramolecular and (b) Intermolecular Associations	11
(4) Schematic illustration of the HM-polymer solution viscosity as a function of polymer concentration. a) HM-polymer and b) unmodified polymer	12
(5) Schematic Illustration of EOR Injection Methods	21
(6) Polymer Flooding Process	26
(7) The Scheme of Preparation for The Polymerizable Surfactants (Surfmers)	58
(8) Mass Spectroscopy of Octadecenylsuccinic Anhydride (ODSA)	63
(9) FT-IR Spectroscopy of Octadecenylsuccinic Anhydride (ODSA)	64
(10) $^1\text{H}$ NMR of ODSA-eo22 Hemiester	65
(11) $^{13}\text{C}$ NMR of ODSA-eo22 Hemiester	66
(12) $^1\text{H}$ NMR of OD-ODS-eo22 Diester	67
(13) $^{13}\text{C}$ NMR of OD-ODS-eo22 Diester	68
(14) $^1\text{H}$ NMR of ODSA-eo22Ac Surfmer	69
(15) $^{13}\text{C}$ NMR of ODSA-eo22Ac Surfmer	70
(16) $^1\text{H}$ NMR of OD-ODS-eo22Ac Surfmer	71