



Ain Shams University
University college for Women
(Arts, Science & Education)

**SYNTHESIS, CHARACTERIZATION AND
POLYMERIZATION OF A NOVEL ACRYLAMIDE**

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of

DOCTOR OF PHILOSOPHY
in
PHYSICAL CHEMISTRY

by

Fatma Ahmed Mahmoud Gomaa

To

Department of Chemistry
University college for Women
(Arts, Science & Education)
Ain Shams University

UNDER SUPERVISION OF:

Prof. Dr. Samia M. Mokhtar

Professor of Physical Chemistry
University College for Women
Ain Shams University, Egypt

Prof. Dr. Maher Z. Elsabee

Professor of Physical Chemistry
Faculty of Science,
Cairo University, Egypt

Dr. Sakina M. Abd-ElAziz

Lecturer of Physical Chemistry
University College for Women
Ain Shams University, Egypt

Ain Shams University

2014



Ain Shams University
University college for Women
(Arts, Science & Education)

APPROVAL SHEET

SYNTHESIS, CHARACTERIZATION AND POLYMERIZATION OF A NOVEL ACRYLAMIDE

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

in

PHYSICAL CHEMISTRY

by

Fatma Ahmed Mahmoud Gomaa

Under Supervision of:

Prof. Dr. Samia M. Mokhtar

Professor of Physical Chemistry
University College for Women
Ain Shams University, Egypt

Prof. Dr. Maher Z. Elsabee

Professor of Physical Chemistry
Faculty of Science,
Cairo University, Egypt

Dr. Sakina M. Abd-ElAziz

Lecturer of Physical Chemistry
University College for Women
Ain Shams University, Egypt

Head of Chemistry Department



Ain Shams University
University college for Women
(Arts, Science & Education)

QUALIFICATION

Student Name : **Fatma Ahmed Mahmoud Gomaa**

Scientific Degree : **M.Sc. (Chemistry)**

Department : **Chemistry**

Faculty : **University College for Women**
(Arts, Science and Education)

University : **Ain Shams**

B.Sc. Graduation Date : **May 2005**

M. Sc. Graduation Date : **October 2010**

Ph.D. Graduation date : **2014**

DEDICATION



TO

MY PARENTS

MY KIDS

and

MY HUSBAND

ABSTRACT

ABSTRACT

SYNTHESIS, CHARACTERIZATION AND POLYMERIZATION OF NOVEL ACRYLAMIDE

Student Name: Fatma Ahmed Mahmoud Gomaa

University College for Women
(Arts, Science and Education), Ain Shams University

Two novel acrylamide monomers 4-(4'-cyanophenoxy) phenyl acrylamide (CPPAM) and 4-(4'-trifluoromethyl) phenoxy N-phenyl acrylamide (FPPAM) were synthesized and characterized by elemental analysis. The free radical- initiated polymerization of CPPAM and FPPAM were carried out in THF and 1,4 dioxane respectively, using azobisisobutyronitrile as initiator. The two monomers and their polymers were investigated by ^{13}C NMR, ^1H NMR and FTIR. The effect of monomer, initiator concentrations and temperature on the rate of polymerization (R_p) was studied. The molecular weight averages ($\overline{M}_w$ and $\overline{M}_n$) and polydispersity index of the poly-FPPAM were determined by gel permeation chromatography and were equal to 411,061, 129,046 and 3.185 respectively. The properties of Poly CPPAM and Poly FPPAM including thermal behavior, thermal stability, photo-stability, solubility and intrinsic viscosity were studied. Moreover, the monomer reactivity ratios for the copolymerization of CPPAM and FPPAM with MMA, VAc and AN were calculated by three different methods. It has been found that the PCPPAM, PFPPAM and the copolymers have high thermal stability.

Keywords: *Fluoropolymers, cyanopolymers, acrylamide, FTIR, NMR, Free-radical polymerization, Copolymerization kinetics, Thermal analysis, Methyl methacrylate, vinyl acetate and acrylonitrile.*

ACKNOWLEDGEMENT

ACKNOWLEDGEMENT

I am deeply thankful to **Allah**, by the grace of whom the progress and success of this work was possible.

It is my great pleasure to cordially express my sincere appreciation of all the efforts provided by **Prof. Dr. Samia M. Mokhtar**, Professor of Physical Chemistry, and Ex. Head of Chemistry Department, University College for Women (Arts, Science and Education), Ain Shams University. I am deeply indebted to you for suggesting the subject and close supervision. You have always had time to listen, discuss and comment on my ideas and manuscripts. I especially appreciate all the time you spent on my work and me during the last intensive months.

I am deeply indebted to **Prof. Dr. Maher Zaki ElSabee** Professor of Physical Chemistry, Faculty of Science, Cairo University for his continuous support, encouragement, fruitful opinions, kind supervision and help during all the phases of achieving the objectives of this thesis.

I would like to express my deepest thanks and gratitude to my supervisor **Dr. Sakina M. Abdel Aziz**; Lecturer of Chemistry; Chemistry Department, University College for Women (Arts, Science and Education), Ain Shams University for her kind supervision, guidance, faithful help, and support during the whole process.

I would like to express my great thanks to all members of the Chemistry Department, University College for Women (Arts, Science and Education, Ain Shams University for their continuous helping and support.

Very special thanks to my father, mother, husband, kids and my brothers and sisters for continuous care, support and encouragement.

Fatma Ahmed Mahmoud Gomaa
Cairo, May 2014

LIST OF CONTENTS

List of Contents

List of Tables	viii
List of Figures	xi
List of Symbols and abbreviations	xviii
Aim of the Work	xx

Chapter One

INTRODUCTION & LITERATURE SURVEY

1.1 Introduction	1
1.2 Fluoropolymers.....	4
1.3 Acrylic Monomers	15
1.3.1 Acrylic Monomers Synthesis.....	15
1.3.2 Polymerization of Acryloylamido Monomers	20
1.3.3 Copolymerization of Acryloyl Amido.....	24
1.3.4 Thermal Stability.....	30

Chapter Two

Materials and Experimental Techniques

2.1 Materials.....	34
2.1.1 Monomers.....	34
2.1.1.1 Preparation of 4-4'-Aminophenoxy Benzonitrile Acrylamide.....	34
2.1.1.2 Preparation 4-(4'-trifluoromethyl) phenoxy acrylamide	37

2.1.1.3 Methyl Methacrylate.....	39
2.1.1.4 Vinyl Acetate.....	39
2.1.1.5 Acrylonitrile.....	39
2.1.2 Initiator.....	39
2.1.3 Solvents.....	39
2.2 Experimental Techniques.....	40
2.2.1 Polymerization Procedure.....	40
2.2.2 Kinetics of Homopolymerization.....	40
2.2.3 Viscosity Measurements.....	41
2.2.3 Gel Permeation Chromatography (GPC)	42
2.2.4 Thermogravimetric Analysis (TGA)	43
2.2.5 Differential Scanning Calorimetric Analysis.....	43
2.2.6 Photo Stability	43
2.2.7 Solubility	43
2.2.8 X-ray Diffraction	43
2.3 Copolymerization.....	44
2.3.1 Copolymerization Process.....	44
2.3.2 Copolymer Analysis.....	44
2.3.3 Calculation of the Reactivity Ratios of the monomers.....	45
2.3.3.1 Fineman-Ross (F-R) method.....	45
2.3.3.2 Kelen-Tudos (K-T) method.....	46
2.3.3.3 Non-Linear Least Square Method (NLLS).....	46
2.3.4 Thermal Analysis.....	47

Chapter Three

Results and Discussion

Part One

Monomers Synthesis, Polymerization and Characterization

3.1 Monomer Synthesis	49
3.2 Homopolymerization of CPPAM and FPPAM.....	56
3.3 Polymerization Kinetics of CPPAM and FPPAM...	57
3.3.1 Dependence of the Rate of Polymerization on Initiator Concentration.....	57
3.3.2 Dependence of the Rate of Polymerization on the Monomer Concentration.....	60
3.3.3 Effect of Temperature on the Rate of Polymerization	62
3.4 Characterization of the Prepared Polymers	66
3.4.1 Viscosity Measurements	66
3.4.2 Gel Permeation Chromatography (GPC).....	74
3.4.3 X-Ray Diffraction (XRD)	74
3.4.4 Solubility	77
3.4.5 Photo Stability of Poly-CPPAM and Poly-FPPAM	78
3.4.6 Thermal Stability.....	80
3.4.6.1 Thermal Analysis of PCPPAM.....	80
3.4.6.2 Thermal Analysis of PFPPAM.....	82

Part Two

Copolymerization of the New Synthesized Monomers

3.5 Copolymerization Behavior of Both CPPAM and FPPAM.....	89
3.5.1 Copolymerization Behavior of 4-(4`-CyanoPhenoxy) Phenyl Acrylamide Monomer (CPPAM).....	89
3.5.2 Copolymerization Behavior of 4-(4`-Trifluoromethyl) Phenoxy N-Phenyl Acrylamide Monomer (FPPAM).....	94
3.6 Characterization of Copolymerization.....	99
3.6.1 Spectral Characterization of Copolymer.....	100
3.6.2 Thermal Behavior of Copolymers.....	103
SUMMARY AND GENERAL CONCLUSIONS.....	113
References.....	115
Arabic Summary.....	128