

Emulsifier Free Emulsion Polymerization in Presence of Some Fine Solid Inorganic Particles

A Thesis

Submitted to

Faculty of Science - Ain- Shams University

By

Mahmoud Essam Abd El-Aziz Shaaban

M.Sc. in Org.Chem. Cairo University, 2009

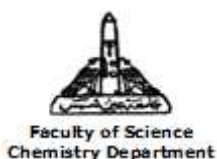
For

The Degree of Ph.D.

in

Organic Chemistry

2014



Emulsifier Free Emulsion Polymerization in Presence of Some Fine Solid Inorganic Particles

A Thesis Submitted to
Faculty of Science, Ain-Shams University

By
Mahmoud Essam Abd El-Aziz Shaaban
M.Sc. Org.Chem. Cairo University, 2009
For

The Degree of Ph.D. in Organic Chemistry

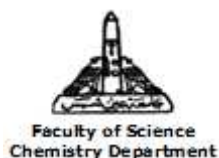
Thesis Supervisors

Prof. Dr. Abd El-Gawad M. Rabie
*Prof. of Polymer Chemistry,
Chemistry Depart, Faculty of Science, Ain Shams University*

Prof. Dr. Abdalla B. Moustafa
*Prof. of polymer Chemistry,
Polymer & Pigments Department,
National Research Center*

Prof. Dr. Hisham A. Essawy
*Prof. of polymer Chemistry,
Polymer & Pigments Department,
National Research Center*

2014



Approval Sheet of the Thesis

Entitled

**Emulsifier Free Emulsion Polymerization in Presence of Some
Fine Solid Inorganic Particles**

Thesis Advisors

Thesis Approved

Prof. Dr. Abd El-Gawad M. Rabie

.....

Chemistry Department, Faculty of Science,
Ain Shams University.

Prof. Dr. Abdalla B. Moustafa

.....

*Polymer & Pigments Department,
National Research Centre*

Prof. Dr. Hisham A. Essawy

.....

*Polymer & Pigments Department,
National Research Centre*

Head of Chemistry Department

Prof. Dr. Hamed Ahmed Younes

ACKNOWLEDGEMENT

First and before all, I would like to thank ALLAH who granted me the ability to perform this thesis and helped me to pass safely through all the difficulties which I thought impossible to overcome.

I wish to express my deep appreciation to Prof Dr. **Abd El-Gawad Mohamed Rabie** Professor of Polymer Chemistry, Faculty of Science, Ain Shams University, for his benevolent supervision and kindly guidance throughout this work, and continuous supervision.

I am very grateful to Prof. Dr. **Abdalla Baker Moustafa**, Prof. Dr. **Hisham Abd El-Fatah Essawy** and Prof. Dr. **Hassen S. Emira**, Professors of Polymer Chemistry, National Research Center, for suggestion of the topic of this work, their precious supervision, continuous effort and help to have this work done.

My thanks are expanded to my colleagues in the Department of Polymers & Pigments, National Research Center, for their cooperation and their help in various ways.

I am profoundly grateful to all staff members of the Chemistry Department, Faculty of Science, Ain Shams University.

Abstract

Name:- Mahmoud Essam Abd El-Aziz

Title:- Emulsifier Free Emulsion Polymerization in Presence of
Some Fine Solid Inorganic Particles

Degree:- Ph. D.

Solid nanoparticles can be used as stabilizers for oil/water (o/w) emulsions instead of the conventional surfactants. In this thesis, styrene was initially ultrasonicated in water in the presence of silica nanoparticles as solid particles stabilizer to induce the formation of stable o/w emulsion in the presence of potassium persulfate (PPS) as a water soluble initiator, under wide range of conditions including the initiator, monomer concentration, content of the silica nanoparticles, pH and temperature. The emulsion stability, morphology and the kinetics for this system were illustrated.

Also, the montmorillonite (Nanofil® 116) was used as solid nanoparticles stabilizer to induce the formation of stable (o/w) emulsion in the presence of PPS. Imaging with transmission electron microscope (TEM) and a field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray (EDX) unit proved the formation of hybrid latex particles

via Pickering mode of emulsification. Furthermore, the thermal gravimetric analysis (TGA) showed the increase in the degradation temperature of polystyrene in the formed composite which proved the formation of protective sheath from silica or montmorillonite surrounding the polystyrene formed.

The prepared nanocomposites (polystyrene/Ludox HS-30 and polystyrene/montmorillonite) were added in different contents (wt%) to polypropylene and ethylene-vinyl acetate copolymer to study their effect on the physico-mechanical properties of these polymers.

Keywords:-

Styrene - Ludox HS-30 - Nanofil® 116 - Pickering emulsion – kinetic study - polystyrene/Ludox HS-30 composite - polystyrene/montmorillonite nanocomposites.

Contents

	Page No.
Aim of the work	I
List of Abbreviations	I I
List of Tables	I I I
List of Figures	V I

Chapter I

<i>1- Introduction</i>	<i>1</i>
1.1 Emulsion polymerization	1
1.2 Stability of Emulsions	1
1.2.1 Stabilization with Surfactants	2
1.2.1.1. Steric hindrance	2
1.2.1.2. Electrostatic repulsion	3
1.2.2 Stabilization with Polymers	3
1.2.3 Stabilization with Particles	4
1.2.3.1 Factors affecting emulsion stability using solid particles	7
1.2.3.1.1 Effect of particles concentration	7
1.2.3.1.2 Effect of particles wettability	8
1.2.3.1.3 Effect of particles size	11
1.2.3.1.4 Effect of particle-particle interaction	11
1.2.3.1.5 Effect of electrolyte	12
1.2.3.1.6 Effect of water-oil ratio	13

1.2.3.2 Advantages of stabilization of emulsions using solid particles (Pickering emulsions)	13
1.2.3.3 The general rules of solid particles -stabilized emulsions	15

Chapter II

2- Literature Review	16
2.1 Pickering emulsion using inorganic solid particles	16
2.2 Pickering emulsion using clay nanoparticles	39
2.3 Pickering emulsion using polymeric nanoparticles	44

Chapter III

Materials and Experimental Techniques	47
3.1 Materials	47
3.2. Methods	47
3.2.1 Preparation of Pickering emulsion	47
3.2.2 Sampling	48
3.2.3 Polymer staining	48
3.3 Measurements and characterizations	49
3.3.1 Gel Permeation Chromatography (GPC)	49
3.3.2. Transmission Electron Microscope (TEM)	50
3.3.3. Field Emission- Scanning Electron Microscope (FE-SEM)	51
3.3.4. Dynamic Light Scattering (DLS)	52
3.3.5. Thermal analysis	52

3.3.6. Infrared spectroscopy	52
3.3.7. Physico-mechanical properties	52
3.3.8. Hardness measurement	52
3.3.9. . XRD Analysis	53
3.4 Theoretical calculations	53
3.4.1 Calculation of the rate of emulsion polymerization (R_p)	53
3.4.2 Calculation of the apparent activation energy	53
<i>Chapter IV</i>	
4- Results and Discussion	55
4.1. Pickering emulsion polymerization of styrene using Ludox HS-30 as solid particles stabilizer	55
4.1.1. Emulsion stability	55
4.1.1.1. Effect of monomer concentration	56
4.1.1.2. Effect of initiator concentration	63
4.1.1.3. Effect of solid particles (Ludox HS-30) concentration	68
4.1.1.3.1. Effect of solid particles (Ludox HS-30) content at styrene concentration 0.435 mol/L	68
4.1.1.3.2. Effect of solid particles (Ludox HS-30) content at styrene concentration 1.304 mol/L	74
4.1.1.4. Effect of pH on the stability of the emulsion	80

4.1.1.4.1. Effect of pH on the stability of the emulsion before polymerization	83
4.1.1.4.2. Effect of pH on the stability of the emulsion after polymerization	87
4.1.2. Thermal gravimetric analysis of the Pickering emulsions	98
4.1.2.1. Effect of the Ludox HS-30 concentration on the thermal degradation of polystyrene/Ludox HS-30 composite	99
4.1.2.2. Effect of pH value on the thermal degradation of polystyrene/Ludox HS-30 composites	101
4.1.3. Characterization with infrared spectroscopy	102
4.1.4. A kinetic study of the Pickering emulsion polymerization of styrene	105
4.1.4.1. Dependence of the rate of polymerization on the monomer concentration	105
4.1.4.2. Dependence of the rate of polymerization on the initiator concentration	109
4.1.4.3. Dependence of the rate of polymerization on the Ludox HS-30 concentration	114
4.1.4.4. Dependence of the rate of polymerization on the pH	119
4.1.4.5. Dependence of the rate of polymerization on the reaction temperature	122

4.2. Pickering emulsion polymerization of styrene using Nanofil® 116 as solid particles stabilizer	125
4.3. Enhancement of the physico-mechanical properties of polypropylene and ethylene vinyl acetate copolymer using polystyrene/Ludox HS-30 and polystyrene/clay nanocomposite	136
4.3.1. Effect of the polystyrene/Ludox HS-30 and polystyrene/clay nanocomposite on the mechanical properties of ethylene vinyl acetate copolymer (EVA)	137
4.3.2. Effect of the polystyrene/Ludox HS-30 and polystyrene/clay nanocomposite on the mechanical properties of polypropylene (PP)	141
Summary and Conclusions	145
References	149