

17.9.69

ORGANOMETALLIC INITIATORS OF  
FREE-RADICAL POLYMERIZATION:

---

A thesis submitted by

GOH TONG HONG, B.Sc.

Candidate for the Degree of

Doctor of Philosophy

in the

Department of Physical and Inorganic

Chemistry, University of Adelaide

---

AUGUST, 1968

| <u>CONTENTS:</u> |   | page |
|------------------|---|------|
| <u>PART I</u>    | <u>GENERAL INTRODUCTION:</u>                    | 1    |
|                  | A. CLASS 1 INITIATORS                           | 2    |
|                  | 1. Anionic Polymerization                       | 2    |
|                  | 2. Free Radical Polymerization                  | 5    |
|                  | B. CLASS 2 INITIATORS                           | 7    |
|                  | 1. Ziegler-Natta Catalysts                      | 7    |
|                  | 2. Free Radical Initiators                      | 8    |
|                  | C. CLASS 3 INITIATORS                           | 10   |
|                  | 1. Metal Carbonyls                              | 10   |
|                  | 2. Metal Acetylacetonates                       | 10   |
|                  | 3. Redox Initiators                             | 15   |
| <br>             |   |      |
| <u>PART II</u>   | <u>INITIATION OF VINYL POLYMERIZATION BY</u>    |      |
|                  | <u>AMMONIUM TRICHLORACETATE IN THE PRESENCE</u> |      |
|                  | <u>OF CUPRIC ACETYLACETONATE</u>                | 19   |
| <br>             |   |      |
| <u>CHAPTER 1</u> | <u>EXPERIMENTAL</u>                             | 19   |
|                  | A. HIGH VACUUM LINE                             | 19   |
|                  | B. MATERIALS                                    | 20   |
|                  | C. DILATOMETERS                                 | 22   |
|                  | 1. Construction                                 | 22   |
|                  | 2. Calibration                                  | 22   |
|                  | 3. Measurement of Conversion                    |      |
|                  | Factors for Monomers                            | 23   |

Contents...continued

|                  |  |           |
|------------------|--|-----------|
| D.               | FILLING OF DILATOMETERS  | 24        |
| E.               | THERMOSTAT   | 26        |
| <b>CHAPTER 2</b> | <b><u>INTRODUCTION, RESULTS AND DISCUSSION</u></b>   | <b>27</b> |
| A.               | INTRODUCTION   | 27        |
| B.               | RESULTS  | 27        |
| 1.               | Dilatometric Measurements of<br>Vinyl Acetate at 65°C  | 32        |
| 2.               | Polymerization of Methyl<br>Methacrylate Initiated by Ammonium<br>Trichloroacetate and Cupric<br>Acetylacetonate | 36        |
| (a)              | Dilatometric Measurements  | 36        |
| (b)              | Conversion-Time Curves   | 37        |
| (c)              | Low Salt Concentrations  | 38        |
| (d)              | High Salt Concentrations   | 40        |
| (e)              | Effects of Each Initiator<br>Component on Methyl Methacrylate<br>Polymerization                                  | 44        |
| C.               | DISCUSSION   | 45        |
| 1.               | High Salt Concentrations   | 45        |
| 2.               | Low Salt Concentrations  | 46        |

Contents...continued

|                                  |    |
|----------------------------------|----|
| (a) Modified Mechanisms          | 46 |
| (b) Alternative Mechanism        | 48 |
| (c) Nature of Linear Termination | 51 |
| (d) A problem about Initiation   | 53 |
| D. SUMMARY                       | 58 |

PART III INITIATION OF VINYL POLYMERIZATION BY  
FERROUS ACETYLACETONATE 59

|   |    |
|---|----|
| <u>CHAPTER 1 EXPERIMENTAL</u>   | 59 |
| A. INTRODUCTION   | 59 |
| B. MATERIALS  | 59 |
| C. DILATOMETER AND FILLING OF<br>DILATOMETER                          | 60 |
| D. THERMOSTAT   | 64 |
| E. CLEANING OF USED DILATOMETERS AND<br>DILATOMETER-FILLING APPARATUS | 65 |

|  |    |
|--|----|
| <u>CHAPTER 2 INITIATION OF POLYMERIZATION OF STYRENE</u><br><u>BY FERROUS ACETYLACETONATE - RESULTS AND</u><br><u>DISCUSSION</u> | 67 |
| A. RESULTS   | 67 |
| 1. Polymerization at 60°C  | 67 |
| 2. Energy of Activation Experiments  | 70 |

**Contents...continued**

|                  |   |           |
|------------------|---|-----------|
| B.               | DISCUSSION  | 73        |
| <b>CHAPTER 3</b> | <b><u>INITIATION OF POLYMERIZATION OF METHYL</u></b>    | <b>80</b> |
|                  | <b><u>METHACRYLATE AND VINYL ACETATE BY FERROUS</u></b> |           |
|                  | <b><u>ACETYLACETONATE - RESULTS AND DISCUSSION:</u></b> |           |
| A.               | RESULTS   | 80        |
| 1.               | Polymerization of Methyl                                |           |
|                  | Methacrylate Initiated by Ferrous                       |           |
|                  | Acetylacetonate   | 80        |
| (a)              | Preliminary Dilatometric                                |           |
|                  | Experiments at 25°C                                     | 80        |
| (b)              | Polymerization at 60°C                                  | 81        |
| (c)              | Energy of Activation                                    |           |
|                  | Experiments   | 83        |
| 2.               | Dilatometric Measurements of                            |           |
|                  | vinyl acetate at 60°C                                   | 87        |
| B.               | DISCUSSION  | 89        |
| 1.               | Low Concentrations of Ferrous                           |           |
|                  | Acetylacetonate   | 89        |
| 2.               | High Concentrations of Ferrous                          |           |
|                  | Acetylacetonate   | 90        |
| 3.               | Intermediate Concentration of                           |           |
|                  | Ferrous Acetylacetonate                                 | 91        |
| C.               | SUMMARY   | 96        |

Contents...continued

|                     |  |     |
|---------------------|--|-----|
| <u>PART IV</u>      | <u>INITIATION OF POLYMERIZATION OF METHYL</u>  |     |
|                     | <u>METHACRYLATE BY FERROUS ACETYLACETONATE</u> |     |
|                     | <u>IN THE PRESENCE OF CUMENE HYDROPEROXIDE</u> | 98  |
| <u>CHAPTER 1</u>    | <u>EXPERIMENTAL:</u>                           | 98  |
|                     | A. INTRODUCTION                                | 98  |
|                     | B. MATERIALS                                   | 99  |
|                     | C. DILATOMETER AND FILLING OF                  |     |
|                     | DILATOMETER                                    | 99  |
| <u>CHAPTER 2</u>    | <u>RESULTS AND DISCUSSION</u>                  | 103 |
|                     | A. RESULTS                                     | 103 |
|                     | 1. Polymerization at 25°C                      | 103 |
|                     | 2. Energy of Activation Experiments            | 107 |
|                     | B. DISCUSSION                                  | 109 |
| <u>PART V</u>       | <u>A. GENERAL CONCLUSIONS</u>                  | 116 |
|                     | B. SUGGESTIONS FOR FURTHER WORK                | 118 |
| <u>PART VI</u>      | <u>APPENDIX</u>                                | 121 |
|                     | DETERMINATION OF NUMBER-AVERAGE MOLECULAR      |     |
|                     | WEIGHT OF POLYMERS FROM OSMOTIC PRESSURE -     |     |
|                     | AN EXTENSION OF PART II.                       |     |
| <u>BIBLIOGRAPHY</u> |  | 129 |

**SYNOPSIS :**

The potentialities of certain organometallic complexes as initiators of free-radical polymerization have been investigated by dilatometric techniques. The systems studied are based on metal(II) acetylacetonates in the absence or presence of a reductant or an oxidizer.

The Bamford initiator, which consists of cupric acetylacetonate and ammonium trichloroacetate, does not initiate the polymerization of vinyl acetate at 65°C. Consequently, the kinetics of polymerization of methyl methacrylate previously investigated by Bamford et.al. at 80°C, have been re-examined at 65°C. The kinetics at 65°C were different from that at 80°C. A modified or alternative mechanism at 65°C, which involves a linear termination reaction in addition to the Bamford mechanism, is discussed together with a problem involved in the initiation process.

Certain acetylacetonato complexes initiate the polymerization of certain monomers by themselves. Ferrous acetylacetonate polymerizes styrene and methyl methacrylate, but not vinyl

acetate. The mechanism in these cases probably involves the formation of a complex between monomer and initiator. The important role of the unassociated or associated form of the ferrous acetylacetonate under various experimental conditions is discussed.

The kinetics of the polymerization of methyl methacrylate at 25°C initiated by a mixture of ferrous acetylacetonate and cumene hydroperoxide are discussed.



This thesis contains no material previously submitted for a degree of diploma in any University and, to the best of my knowledge and belief, contains no material previously written by another person, except when due reference is made in the text.



GOH TONG HONG

ACKNOWLEDGEMENT:

I wish to express my sincere gratitude to my supervisor, Dr. P.E.M. Allen for his unfailing support, constant encouragement and constructive advice during the course of this investigation. I would like to thank Professor D.O. Jordan for his continual interest.

I would also like to thank: Messrs. G. Duthie and T. Trivett for their assistance in constructing the glassware in this project; Messrs. A. Bowers and A. Lloyd of the general workshop, and Messrs. K. Shepherdson and A. Moller of the electronic workshop for their help in construction and maintenance of apparatus; Miss A. Whittle for preparing the photographs for this thesis; Mr. J. Cecchin for assistance in reprecipitating and freeze drying the polymers; Mr. W. Dankiw for carrying out the molecular weight measurements; other members of the staff and fellow research colleagues for many stimulating discussions.

Finally, I am indebted to the University of Adelaide for providing me with a Research Grant during the duration of this work.