

## TABLE OF CONTENTS

	<b>Page</b>
TABLE OF CONTENTS .....	i
LIST OF TABLES .....	iii
LIST OF FIGURES .....	iv
INTRODUCTION .....	1
Objective .....	3
Scope of Thesis .....	3
LITERATURE REVIEW .....	4
Experimental Investigations .....	4
Computational Investigations .....	6
MATERIALS AND METHODS .....	9
Theoretical Background .....	9
Polymer Crystallization .....	9
Modeling of Morphology Evolution and Crystallization	
Kinetics .....	14
Algorithm for studying effect of number of predetermined nuclei	
and growth rate .....	19
Algorithm for studying effect of crystallization temperature .....	24
Assumptions of the algorithm .....	28
RESULTS AND DISCUSSION .....	30
Effect of Number of Predetermined Nuclei and Growth Rate .....	30
Crystallization Kinetics .....	30
Morphological Development .....	34
Effect of Nucleation .....	34
Effect of Growth Rate .....	38
Effect of Crystallization Temperature .....	42
Crystallization Kinetics .....	44
Morphological Development .....	50

## TABLE OF CONTENTS (Cont'd)

	<b>Page</b>
CONCLUSION.....	57
Effect of Number of Predetermined and Growth Rate.....	57
Effect of Crystallization Temperature.....	57
LITERATURE CITED.....	59
APPENDIX.....	61
Appendix A.....	62
Appendix B.....	66

## LIST OF TABLES

Table		Page
1	Interpretation of Avrami Coefficients.....	15
2	Values of parameters for study the effect of number of predetermined nuclei and growth rate.....	23
3	Values of parameters for study the effect of crystallization temperature.....	28
4	Comparison results between simulation and experiment.....	49

## LIST OF FIGURES

Figure	Page
1 Comparison between the final morphology obtained from (a) polarized light microscope (PLM) and (b) simulation.....	2
2 Polymer chain arrangement in spherulite form: (a) 2-dimensions and (b) 3-dimensions.....	10
3 Number of nuclei versus time during the crystallization of poly (trimethylene terephthalate) at several crystallization temperatures.....	11
4 The spherulites size as a function of time during crystallization of poly (trimethylene terephthalate) at several crystallization temperatures.....	12
5 Spherulite growth rate at various crystallization temperatures for poly (trimethylene terephthalate). Dots are experimental results and line is Lauritzen-Hoffman model.....	12
6 Simplified algorithm for our stochastic simulation (Effect of number of predetermined nuclei and growth rate) .....	21
7 Examples of polymer morphology obtained from the stochastic simulation ( $N = 10$ and $G = 3$ unit cell/sec) at different crystallization times: (a) $t = 0$ sec, (b) $t = 20$ sec, (c) $t = 40$ sec, and (d) final morphology.....	22
8 Simplified algorithm for our stochastic simulation (Effect of crystallization temperature).....	25
9 Calculation of growth rate ( $G$ ) and number of predetermined nuclei ( $N$ ) by using experimental results for s-PP.....	26
10 Examples of polymer morphology obtained from the stochastic simulation ( $T_c = 85^\circ\text{C}$ ) at different crystallization times: (a) $t = 0$ sec, (b) $t = 20$ sec, (c) $t = 40$ sec, and (d) final morphology.....	27

## LIST OF FIGURES (Cont'd)

Figure		Page
11	Crystallization kinetics for various numbers of nuclei (a) simulated kinetics of area occupied by spherulites and (b) simulated kinetics in logarithm scale. Symbols: simulation results; Lines: theoretical results from the Avrami equation. ....	31
12	Crystallization kinetics at various growth rates. (a) simulated kinetics of area occupied by spherulites and (b) simulated kinetics in logarithm scale. Symbols: simulation results; Lines: theoretical results from the Avrami equation. ....	32
13	Relative crystallinity as a function of time. Dark symbols: results from simulation in this work, open symbols are results from the literature and line are results from Avrami equation (Eq. (4)). ....	33
14	Avrami parameters estimated from simulation results obtained at various numbers of nuclei. Lines are to aid eye only. ....	33
15	Avrami parameters estimated from simulation results obtained at various growth rate. Lines are to aid eye only. ....	34
16	Time evolution of distributions of spherulite size for three different numbers of nuclei: (a) 50 nuclei, (b) 100 nuclei, and (c) 500 nuclei. ....	36
17	Frequency distributions of spherulite size for three different numbers of nuclei at (a) $t = 60$ sec and (b) final morphology. ....	37
18	The average spherulite size as a function of time for various numbers of nuclei. ....	38
19	Time evolution of distributions of spherulite size for three different growth rates: (a) 1 pixel/s, (b) 3 pixels/s, and (c) 5 pixels/s. ....	40
20	Frequency distributions of spherulite size for three different growth rates at (a) $t = 14$ sec and (b) final morphology. ....	41

## LIST OF FIGURES (Cont'd)

Figure		Page
21	The average spherulite size as a function of time for various growth rates. ....	42
22	The effect of crystallization temperature on growth rate of spherulite, $G$ , Avrami rate constant, $k_A$ , and nucleation density, $N$ . ....	43
23	Crystallization kinetics at various crystallization temperatures in the range of $65^{\circ}C \leq T_c \leq 85^{\circ}C$ . (a) simulated kinetics of area occupied by spherulites and (b) simulated kinetics in logarithm scale. Symbols: simulation results; Lines: theoretical results from the Avrami equation. ....	45
24	Crystallization kinetics at various crystallization temperatures in the range of $40^{\circ}C \leq T_c \leq 60^{\circ}C$ . (a) simulated kinetics of area occupied by spherulites and (b) simulated kinetics in logarithm scale. Symbols: simulation results; Lines: theoretical results from the Avrami equation. ....	45
25	Avrami parameters (a) Avrami rate constant ( $k_A$ ) and (b) Avrami exponential ( $n_A$ ) estimated from simulation results obtained at various crystallization temperatures. Lines are to aid eye only. ....	47
26	Method for validation of algorithm developed in this work with reported experimental data. ....	48
27	Comparison of Avrami rate constant between simulation results and experimental results. ....	48
28	Comparison between crystallization half-time obtained from simulation and crystallization half-time reported earlier from experiment of Supphol. ....	49

## LIST OF FIGURES (Cont'd)

Figure		Page
29	Time evolution of distributions of spherulite size for different crystallization temperatures: (a) $T_c=40^\circ\text{C}$ , (b) $T_c=50^\circ\text{C}$ , (c) $T_c=60^\circ\text{C}$ , (d) $T_c=70^\circ\text{C}$ , (e) $T_c=80^\circ\text{C}$ and (f) $T_c=90^\circ\text{C}$ .....	52
30	Final distributions of spherulite size at various crystallization temperatures.....	55
31	Evolution of spherulite size at various crystallization temperatures.	56
32	Effect of crystallization temperature on final average spherulites size.	56

### Appendix Figure

A1	Relative crystallinity as a function of time obtained from different numbers of run.....	63
A2	Frequency of spherulites size at time 36 and various numbers of runs.....	64
A3	Frequency of spherulites size at time 36 and various mesh sizes.	65
B1	The main window of Polymer Crystallization Program for study effect of number of predetermined nuclei and growth rate.....	68
B2	Outputs of the program in spreadsheet format.....	69
B3	Outputs of the program in graphical format.....	70
B4	The main window of Polymer Crystallization Program for study effect of crystallization temperature. ....	71
B5	Outputs of the program in spreadsheet format.....	72
B6	Outputs of the program in graphical format.....	73