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**KINETICS OF THERMAL-INITIATED FREE RADICAL  
COPOLYMERIZATION OF  
STYRENE AND METHYL METHACRYLATE**

**Miss Naporn Santisampan**

**A Thesis submitted in Partial Fulfillment of the Requirements  
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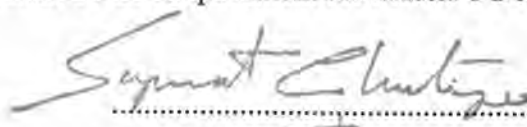
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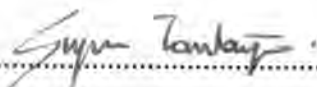
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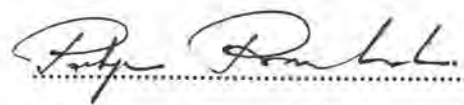
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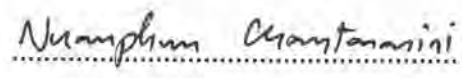
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นพร สันติสัมพันธ์ : จลนพลศาสตร์ของฟรีเรดิคัลโคพอลิเมอไรเซชันของสไตรีนและเมทิลเมทาคริเลตริเริ่มด้วยความร้อน (KINETICS OF THERMAL-INITIATED FREE RADICAL COPOLYMERIZATION OF STYRENE AND METHYL METHACRYLATE) อ. ที่ปรึกษา : ศ.ดร. ภัทรพรณ ประศาสน์สารกิจ, อ. ที่ปรึกษาร่วม : ดร. อนุชา เอื้อเพิ่มเกียรติ, 91 หน้า, ISBN 974-638-596-8.

งานวิจัยนี้ได้ศึกษาจลนพลศาสตร์ของปฏิกิริยาโฮโมพอลิเมอไรเซชันของสไตรีนและเมทิลเมทาคริเลตริเริ่มด้วยความร้อนโดยใช้ 2,2'-เอโซบิส(ไอโซบิวทีโรไนไตรล์) (AIBN) เป็นตัวริเริ่มปฏิกิริยา โดยใช้เทคนิคดีฟเฟอร์เรนเชียลสแกนนิ่งคาลอริมิตรี (DSC) ในการวัดความร้อนที่เกิดขึ้นขณะเกิดปฏิกิริยาพอลิเมอไรเซชัน ซึ่งนำมาใช้ในการหาการเปลี่ยนของโมโนเมอร์ต่อเวลาในการเกิดปฏิกิริยาต่างๆกัน อันดับปฏิกิริยา (reaction order) ของพอลิเมอไรเซชันของสไตรีนและเมทิลเมทาคริเลต ที่อุณหภูมิ 80°C เมื่อเทียบกับความเข้มข้นของตัวริเริ่มปฏิกิริยามีค่าเท่ากับ 0.33 และ 0.53 ตามลำดับ ค่าพลังงานกระตุ้น (Activation energy) ของพอลิเมอไรเซชันของสไตรีนและเมทิลเมทาคริเลต มีค่าเท่ากับ 85.0 และ 83.6 กิโลจูลต่อโมล ตามลำดับ และค่าปัจจัยการชนของพอลิเมอไรเซชันของสไตรีนและเมทิลเมทาคริเลต มีค่าเท่ากับ  $2.84 \times 10^9$  และ  $4.88 \times 10^9$  (ลิตร)<sup>1/2</sup>ต่อ(โมล)<sup>1/2</sup>ต่อวินาที ตามลำดับ

การศึกษาจลนพลศาสตร์ของโคพอลิเมอไรเซชันของสไตรีนและเมทิลเมทาคริเลต ที่ 60°C โดยใช้องค์ประกอบของโคโมโนเมอร์ (comonomer composition) อยู่ในช่วง 0.2-0.6 สัดส่วนโดยโมลของสไตรีน พบว่าค่าคงที่อัตรา (propagation rate constant) สำหรับปฏิกิริยาโคพอลิเมอไรเซชันที่ใช้องค์ประกอบของโคโมโนเมอร์ 0.2 0.4 และ 0.6 สัดส่วนโดยโมลของสไตรีน มีค่าเท่ากับ 689 625 และ 498 ลิตรต่อโมลต่อวินาที ตามลำดับ ค่าอัตราส่วนความว่องไวโมโนเมอร์ (monomer reactivity ratio) ของสไตรีนและเมทิลเมทาคริเลตอยู่ในช่วง 0.40-0.48 และ 0.08-0.50 ตามลำดับ การใช้เทคนิคกาซโครมาโตกราฟีเพื่อยืนยันผลจาก DSC พบว่า เทคนิคทั้งสองให้ผลไม่แตกต่างกันมากนัก โดยมีค่าความคลาดเคลื่อนสัมพัทธ์อยู่ในช่วง 0.01-3.58% และ 2.24-9.10% สำหรับปฏิกิริยาโฮโมพอลิเมอไรเซชันและโคพอลิเมอไรเซชันตามลำดับ

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ลายมือชื่ออาจารย์ที่ปรึกษา .....  
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KEY WORD: KINETICS / MONOMER REACTIVITY RATIO / DSC / STYRENE / METHYL METHACRYLATE

NAPORN SANTISAMPAN : KINETICS OF THERMAL-INITIATED FREE RADICAL COPOLYMERIZATION OF STYRENE AND METHYL METHACRYLATE. THESIS ADVISOR : PROF. PATTARAPAN PRASASSARAKICH, Ph.D., THESIS CO-ADVISOR : ANUCHA EUAPERMKIATI, Ph.D. 91 pp. ISBN 974-638-596-8.

The kinetics of thermal-initiated of homopolymerization of styrene and methyl methacrylate (MMA) using 2,2'-azobisisobutyronitrile (AIBN) as initiator were studied. Differential scanning calorimetry (DSC) technique was employed to detect the heat evolved during the polymerization which was used to calculate the monomer conversion at particular time. The reaction order of polymerization of styrene and MMA at 80°C with respect to the initiator concentration was 0.33 and 0.53, respectively. The activation energy of the polymerization of styrene and MMA was 85.0 and 83.6 kJ/mol, respectively. The frequency factor of the polymerization of styrene and MMA was  $2.84 \times 10^9$  and  $4.88 \times 10^9 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$ , respectively.

The kinetics of copolymerization of styrene and MMA were studied at 60°C with the variation of feed monomer composition in the ranges of 0.2-0.6 mole fraction of styrene. The value of  $k_p$  of the copolymerization using the comonomer having 0.2, 0.4 and 0.6 mole fraction of styrene were 689, 625, 498  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , respectively. The reactivity ratio of styrene and MMA was in the range of 0.40-0.48 and 0.08-0.50. Gas chromatography was employed to confirm the DSC technique. The data from both techniques were not much different. The relative error of two methods was in the ranges of 0.01-3.58% and 2.24-9.10% for homopolymerization and copolymerization, respectively.

ภาควิชา.....

สาขาวิชา.....

ปีการศึกษา..... ๒๕๔๐

ลายมือชื่อนิสิต..... นพพร สันตีสัมปาน

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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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## LIST OF ABBREVIATIONS

- $a_t$  The accumulated area under the isothermal DSC curve from the initial time to time  $t$
- $A$  Frequency or pre-exponential factor
- AIBN 2,2'-Azo(bis)isobutyronitrile
- $A_T$  The total peak area for the monomer conversion up to 100%
- $-\frac{d[M]}{dt}$  Rate of monomer disappearance.
- DSC Differential scanning calorimetry
- $\delta$  The reciprocals of  $k_p/(2k_t)^{1/2}$  ratio for the homopolymerizations of the individual monomers
- $\Delta H_I$  The total heat of isothermal polymerization
- $\Delta H_P$  The total heat of polymerization
- $\Delta H_R$  The total heat of polymerization of the residual monomer
- $E_a$  The activation energy
- $f$  The initiator efficiency
- $f_1$  Mole fraction of unreacted monomer  $M_1$  in the feed monomer composition
- $F_1$  Mole fraction of monomer  $M_1$  in the increment of copolymer formed
- GC Gas chromatography
- $[I]$  Initiator concentration
- $[I]_0$  Initial concentration of initiator
- $k_{11}$  Rate constant for the addition of monomer ( $M_1$ ) to the propagating radical ( $\sim M_1^{\cdot}$ )
- $k_{12}$  Rate constant for the addition of monomer ( $M_2$ ) to the propagating radical ( $\sim M_1^{\cdot}$ )
- $k_{21}$  Rate constant for the addition of monomer ( $M_1$ ) to the propagating radical ( $\sim M_2^{\cdot}$ )
- $k_{22}$  Rate constant for the addition of monomer ( $M_2$ ) to the propagating radical ( $\sim M_2^{\cdot}$ )



## LIST OF ABBREVIATIONS (continued)

$k_d$	Rate constant for the initiator dissociation
$k_i$	Rate constant for the initiation step
$k_{ov}$	The overall rate constant
$k_p$	Rate constant for the propagation step
$k_t$	Rate constant for the termination step
$k_{t11}$	Rate constant for the termination between radicals having similar terminal structure ( $\sim M_1\cdot$ )
$k_{t12}$	Rate constant for the termination between the unlike radicals
$k_{tp}$	Rate constant for the primary termination
$m_r$	Weight of residual monomer determined by GC technique
$m_i$	Initial weight of the reaction mixture used in DSC measurement
[M]	Monomer concentration
[M $\cdot$ ]	Concentration of all chain radicals
MMA	Methyl methacrylate
$\phi$	The ratio of half the cross-termination rate constant to the geometric mean of the rate constants for self-termination of like radicals
$r$	Monomer reactivity ratio
R	The residual monomer content
R $\cdot$	Polymer radical
$R_d$	Rate of producing primary radicals
$R_i$	Rate of the initiation step
$R_p$	Rate of the propagation step
$R_{p,0}$	Initial rate of polymerization
w/w	Weight by weight
x	Monomer conversion at time t