# PREPARATION OF POLYMETHACRYLIC ACID-*BLOCK*-POLYSTYRENE PARTICLES BY SELF-ASSEMBLY MECHANISM IN EMULSION POLYMERIZATION

SAWITREE SUE-ENG

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE
PROGRAM IN INNOVATIVE CHEMISTRY
FACULTY OF SCIENCE AND TECHNOLOGY
RAJAMANGALA UNIVERSITY OF TECHNOLOGY THANYABURI
ACADEMIC YEAR 2018

# PREPARATION OF POLYMETHACRYLIC ACID-*BLOCK*-POLYSTYRENE PARTICLES BY SELF-ASSEMBLY MECHANISM IN EMULSION POLYMERIZATION

**SAWITREE SUE-ENG**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE
PROGRAM IN INNOVATIVE CHEMISTRY
FACULTY OF SCIENCE AND TECHNOLOGY
RAJAMANGALA UNIVERSITY OF TECHNOLOGY THANYABURI
ACADEMIC YEAR 2018

**Thesis Title** Preparation of Polymethacrylic Acid-*Block*-Polystyrene Particles by Self-assembly Mechanism in Emulsion Polymerization
**Name – Surname** Miss Sawitree Sue-eng
**Program** Innovative Chemistry
**Thesis Advisor** Assistant Professor Amorn Chaiyasat, Ph.D.
**Thesis Co-advisor** Assistant Professor Preeyaporn Chaiyasat, Ph.D.
**Academic Year** 2018

---

**THESIS COMMITTEE**

S. Kaewpirom ……………………Chairman of the board
(Associate Professor Supranee Kaewpirom, Ph.D.)

Chatchai Ponchio ……………………Committee
(Assistant Professor Chatchai Ponchio, D.Eng.)

P. Chaiyasat ……………………Committee
(Assistant Professor Preeyaporn Chaiyasat, Ph.D.)

A. Chaiyasat ……………………Committee
(Assistant Professor Amorn Chaiyasat, Ph.D.)

Approved by the Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi in Partial Fulfillment of the Requirements for the Master's Degree

Nipat Jongsawat …………… Dean of Faculty of Science and Technology
(Assistant Professor Nipat Jongsawat, Ph.D.)
Date 30 Month April Year 2019

**Thesis Title** Preparation of Polymethacrylic Acid-*Block*-Polystyrene Particles by Self-assembly Mechanism in Emulsion Polymerization
**Name – Surname** Miss Sawitree Sue-eng
**Program** Innovative Chemistry
**Thesis Advisor** Assistant Professor Amorn Chaiyasat, Ph.D.
**Thesis Co-advisor** Assistant Professor Preeyaporn Chaiyasat, Ph.D.
**Academic Year** 2018

## ABSTRACT

The purpose of this research was to study the preparation of polymethacrylic acid-*block*-polystyrene (PMAA-*b*-PS) particles by self-assembly mechanism in the emulsifier-free emulsion polymerization using polymethacrylic acid-iodide (PMAA-I) as a macro chain transfer agent and an emulsifier for preventing particle coagulation.

The first success of emulsifier-free emulsion iodine transfer polymerization (emulsion ITP) of styrene with self-assembly nucleation was carried out as follows: firstly, PMAA-I as a macro chain transfer agent was synthesized by solutions of iodine transfer and reversible chain transfer catalyzed polymerizations (solution ITP and RTCP) with iodoform as a chain transfer agent and germanium iodide as a catalyst (for solution RTCP) in dioxane. Secondly, a dioxane solution of PMAA-I obtained was used for emulsion ITP of polystyrene in alkaline aqueous solution (pH~9). The stable emulsion was obtained without coagulation. At 100% conversion, the number-average diameter was 223 nm. Number-average molecular weight ($M_n$) increased linearly with monomer conversion which was well closed to theoretical $M_n$. However, molecular weight distribution (MWD; $M_w/M_n$) at 100% conversion was still quite high (2.1). During emulsion polymerization, a large amount of unreacted iodoform in PMAA-I solution was occurred as precipitation of iodoform in the alkaline aqueous phase. To improve MWD, PMAA-I prepared by solution ITP was purified before using it in emulsion ITP. In addition, various amounts of iodoform were added into emulsion ITP after the induction period of polymerization (at 90 min). At 1.71 mmol of iodoform, PMAA-*b*-PS particles were produced with good control where $M_w/M_n$ was quite narrow (approximately 1.2). Moreover, the livingness of the obtained polymer was still maintained as the molecular weight and increased with the monomer conversion.

It can be concluded that stable submicrometer-sized of PMAA-*b*-PS particles with narrow MWD were successfully prepared using purified PMAA-I as a macro chain transfer agent with the addition of iodoform at 1.71 mmol after an induction period of polymerization in emulsion ITP.

**Keywords:** iodine transfer polymerization (ITP), reversible chain transfer catalyzed polymerization (RTCP), emulsion polymerization, self-assembly nucleation

**หัวข้อวิทยานิพนธ์** การเตรียมอนุภาคพอลิเมทาคริลิค แอซิด-*บล็อก*-พอลิสไตรีน ด้วยกลไกการประกอบตัวเองในกระบวนการสังเคราะห์พอลิเมอร์แบบอิมัลชัน
**ชื่อ-นามสกุล** นางสาวสาวิตรี เสือเอ็ง
**สาขาวิชา** เคมีนวัตกรรม
**อาจารย์ที่ปรึกษาหลัก** ผู้ช่วยศาสตราจารย์อมร ไชยสัตย์, Ph.D.
**อาจารย์ที่ปรึกษาร่วม** ผู้ช่วยศาสตราจารย์ปรียาภรณ์ ไชยสัตย์, Ph.D.
**ปีการศึกษา** 2561

## บทคัดย่อ

งานวิจัยนี้ มีวัตถุประสงค์ เพื่อศึกษาการเตรียมอนุภาคพอลิเมทาคริลิค แอซิด-*บล็อก*-พอลิสไตรีน ด้วยกลไกการประกอบตัวเองในกระบวนการสังเคราะห์พอลิเมอร์แบบอิมัลชัน โดยใช้พอลิเมทาคริลิค แอซิด-ไอโอไดด์ เป็นสารโยกย้ายสายโซ่มหภาคและสารลดแรงตึงผิวป้องกันการรวมตัวของอนุภาค

ได้ประสบผลสำเร็จเป็นครั้งแรกในการสังเคราะห์พอลิเมอร์ด้วยกลไกไอโอดีน ทรานสเฟอร์แบบอิมัลชันที่ไม่ใช้สารลดแรงตึงผิว (อิมัลชัน ไอทีพี) ของสไตรีน ด้วยการเกิดอนุภาคแบบประกอบตัวเองซึ่งมีขั้นตอน ดังนี้ ในขั้นตอนแรกทำการสังเคราะห์ พอลิเมทาคริลิค แอซิด-ไอโอไดด์ ด้วยการสังเคราะห์พอลิเมอร์แบบสารละลายด้วยกลไกแบบไอโอดีน ทรานสเฟอร์และ รีเวิร์สซิเบิลเชนทรานสเฟอร์ แคตาลิส (โซลูชัน ไอทีพี และ อาร์ทีซีพี) ที่ใช้ไอโอโดฟอร์ม เป็นสารโยกย้ายสายโซ่และเจอร์มาเนียม ไอโอไดด์เป็นตัวเร่งปฏิกิริยา (สำหรับโซลูชัน อาร์ทีซีพี) ในไดออกเซน ในขั้นตอนที่สองนำสารละลาย พอลิเมทาคริลิค แอซิด-ไอโอไดด์ ที่ได้ มาใช้ในการสังเคราะห์พอลิสไตรีนด้วยอิมัลชัน ไอทีพี ในน้ำที่สภาวะเบส (พีเอช ประมาณ 9) ได้อิมัลชันที่มีความเสถียรและไม่รวมตัวกัน ที่ 100 เปอร์เซ็นต์การเปลี่ยนมอนอเมอร์เป็นพอลิเมอร์ มีขนาดของอนุภาคเฉลี่ยโดยจำนวน 223 นาโนเมตร น้ำหนักโมเลกุลเฉลี่ยโดยจำนวนเพิ่มขึ้นเป็นเส้นตรงกับการเปลี่ยนมอนอเมอร์เป็นพอลิเมอร์และมีค่าใกล้เคียงกับน้ำหนักโมเลกุลเฉลี่ยทางทฤษฎี อย่างไรก็ตาม การกระจายตัวของน้ำหนักของพอลิเมอร์ที่ 100 เปอร์เซ็นต์การเปลี่ยนมอนอเมอร์เป็นพอลิเมอร์ค่อนข้างสูง (2.1) ซึ่งพบว่า ระหว่างการสังเคราะห์พอลิเมอร์ในระบบอิมัลชัน มีไอโอโดฟอร์มจำนวนมากในสารละลายของพอลิเมทาคริลิค แอซิด-ไอโอไดด์ ที่ไม่เกิดปฏิกิริยา ดังมีการตกตะกอนในวัฏภาคน้ำที่เป็นเบส ในการปรับปรุงการกระจายตัวของน้ำหนักโมเลกุลของพอลิเมอร์ จะทำบริสุทธิ์ของพอลิเมทาคริลิค แอซิด-ไอโอไดด์

ก่อนนำไปใช้ในการสังเคราะห์ อิมัลชัน ไอทีพี นอกจากนี้ไอโอโฟอร์มที่ปริมาณต่างๆจะถูกเติมลงในระบบการสังเคราะห์ อิมัลชัน ไอทีพี หลังจากผ่านช่วงต้นของการสังเคราะห์พอลิเมอร์ (ที่ 90 นาที) โดยพบว่า การใช้ไอโอโดฟอร์ม ที่ 1.71 มิลลิโมล อนุภาคพอลิเมทาคริลิค แอซิด-*บล็อก*-พอลิสไตรีน จะมีการควบคุมที่ดีโดยมีค่าการกระจายตัวของน้ำหนักโมเลกุลของพอลิเมอร์ค่อนข้างแคบ ( ประมาณ 1.2) นอกจากนี้ พอลิเมอร์ที่ได้ยังแสดงถึงการมีชีวิต โดยน้ำหนักโมเลกุลจะเพิ่มตามการเปลี่ยนมอนอเมอร์ไปเป็นพอลิเมอร์

สามารถสรุปได้ว่า อนุภาคพอลิเมทาคริลิค แอซิด-*บล็อก*-พอลิสไตรีน ขนาดต่ำกว่าไมโครเมตรที่มีความเสถียรและมีการกระจายตัวของน้ำหนักโมเลกุลที่แคบ สามารถเตรียมได้โดยใช้พอลิเมทาคริลิค แอซิด-ไอโอไดด์ ที่ทำให้บริสุทธิ์ เป็นสารโยกย้ายสายโซ่มหภาค พร้อมทั้งเติมไอโอโดฟอร์มที่ 1.71 มิลลิโมล หลังจากช่วงเริ่มต้นของการสังเคราะห์ อิมัลชัน ไอทีพี

**คำสำคัญ:** ไอโอดีนทรานสเฟอร์พอลิเมอร์ไรเซชัน รีเวิร์สซิเบิลเชนทรานสเฟอร์แคตาลิสพอลิเมอร์ไรเซชัน อิมัลชันพอลิเมอร์ไรเซชัน การเกิดอนุภาคแบบประกอบตัวเอง

# Acknowledgements

I would like to take this opportunity to express my gratitude to all people who have made the accomplishment of the thesis. I am profoundly grateful to my advisor, Assistant Professor Dr. Amorn Chaiyasat for advise me with excellent knowledge. He has always teach me whenever I had a trouble and a question about my research and thesis writing. He consistently allowed this work to be my own work but directed me in the right way whenever I need it. I also would like to special thanks to my co-advisors Assistant Professor Dr. Preeyaporn Chaiyasat and Professor Dr. Masayoshi Okubo for giving a valuable advice. In addition, I would like to acknowledge Assistant Professor Dr. Chatchai Ponchio and Associate Professor Dr. Supranee Kaewpirom as thesis committees for their very valuable comments and suggestions on this thesis.

I would like to thank the laboratory of Polymer Colloids, Department of Chemistry, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, and University of Pau and Pays de l'Adour to provide me with various instrument including chemical and equipment throughout my years of study. Thanks to all staffs of the Department of Chemistry, and also really thankful to all members of Polymer Colloids Laboratory for friendly talk and help.

Finally, I would like to express my very profound gratitude to my parents and my family. This accomplishment would not have been possible without them.

Sawitree Sue-eng

## Table of Contents

# List of Tables

## List of Tables (continued)

# List of Figure

## List of Figure (continued)

## List of Figure (continued)

## List of Figure (continued)

## List of Figure (continued)

**Page**

## List of Figure (continued)

**Page**

## List of Figure (continued)

## List of Abbreviations

| | |
|---|---|
| CRP | Conventional radicals polymerization |
| CLRP | Controlled/living radical polymerizations |
| MWD | Molecular weight distributions |
| PRE | Persistent radical effect |
| DT | Degenerative transfer |
| NMP | Nitroxide-mediated polymerization |
| ATRP | Atom transfer radical polymerization |
| RAFT | Reversible addition-fragmentation chain transfer |
| TERP | Organotellurium-mediated living radical polymerization |
| ITP | Iodine transfer polymerization |
| RTCP | Reversible chain transfer catalyzed polymerization |
| PMAA-*b*-PS | Polymethacrylic acid-*block*-polystyrene |
| PMAA-I | Polymethacrylic acid-iodide |
| $CHI_3$ | Iodoform |
| $GeI_4$ | Germanium (VI) iodide |
| $k_{ex}$ | degenerative chain transfer rate constant ($M^{-1}s^{-1}$) |
| $k_{act}$ | activation rate constant ($M^{-1}s^{-1}$) |
| $k_{aeact}$ | deactivation rate constant ($s^{-1}$) |
| MW | Molecular weight |
| $M_n$ | Number-average molecular |
| $M_w$ | Weight-average molecular |
| $d_w$ | Weight-average size diameters |
| $d_n$ | Number-average size diameters |
| $N_p$ | Number of particle |
| $R_p$ | Rate of polymerization |

# CHAPTER 1
# INTRODUCTION

## 1.1 Important and background of thesis

In recent year, the polymer particles have been used in various applications such as paints, paper, and coatings [1]. In general, polymerization process can be classified as the homogeneous and heterogeneous systems. The latter case is more famous than the first one because homogeneous system normally represents gel effect during the polymerization for bulk and using organic solvent for solution polymerizations [2]. In contrast, heterogeneous system can overcome these drawbacks due to using aqueous medium which environmentally friendly. In addition, the molecular weight of the obtained polymer polymerized by this system is always higher than that of the homogeneous system [3, 4]. It is due to the polymerization loci located in the confine space of the polymer particle in which the termination rate is significantly reduced compared with the homogeneous system. Normally, the obtained products as the polymer particles were dispersed in aqueous medium representing the environmental friendly technique. Radical polymerization is the main mechanism used in the heterogeneous system, because it is tolerant to impurities and compatible with water [5]. However, the major limitation of conventional radical polymerization (CRP) is the impossibility to prepare block copolymers, polymers with narrow molecular weight distributions (MWDs), more complex macromolecule architectures and well-defined polymers. To overcome these drawbacks, controlled/living radical polymerizations (CLRPs) [6, 7] have been developed. The main technique of CLRPs are nitroxide-mediated polymerization (NMP) [8-10] , atom transfer radical polymerization (ATRP) [11-13] , reversible addition fragmentation chain transfer (RAFT)[14-17] and organotellurium-mediated living radical polymerization (TERP) [18-20].

Iodine transfer polymerization (ITP) [21-24] is also one of the most famous CLRP techniques because it is simply a method without the utilization of metal. The iodide compounds are used as a chain transfer agent in ITP system such as cyanopropyl iodide and iodoform ($CHI_3$) because it is a commercially available and cheap. Thus, a variety of kinds of techniques developed of polymerization from the ITP system to the obtained well-defined polymer with a narrow MWD has been interested until now. However, for the ITP system having low rate of exchange constant ($k_{ex}$) of iodine chain transfer agent, the synthesized polymer may present low controlled MWD. To overcome this drawback, Goto and coworkers have improved ITP by the addition of a few iodide compounds as a catalyst such as germanium into the ITP system, which was named reversible chain transfer catalyzed polymerization (RTCP) [25]. The rate constant of RTCP is faster than that of ITP which resulted in the formation of polymers with better controlled MWD.

CLRPs have been firstly developed in homogeneous system [26] such as bulk [27] and solution polymerizations [28]. Thereafter, they have been applied to aqueous dispersed systems [29] such as dispersion [30], suspension [31], miniemulsion [32], microemulsion [33] , and emulsion polymerizations [34]. For industrial applications, the most famous technique is an emulsion polymerization because it present high rate of heat transfer during the polymerization, using nontoxic with environmental friendly media and giving higher molecular weight of the obtained polymer [1]. However, the emulsion controlled/living radical polymerization (emulsion CLRP) firstly study was unsuccessfully [34-36] because most of control agents of CLRP are hydrophobic compounds. They mainly partition in the monomer droplets and do not smoothly transfer from the monomer droplets to micelles resulting in low control of the polymerization giving the polymer with broad MWDs. Thereafter, Hawkett, Gilbert, and coworkers proposed a clever idea of the particle formation in an emulsion CLRP which was named self-assembly nucleation [37, 38]. Water-soluble control agent with several units of acrylic acid was firstly dissolved in the aqueous medium. When the hydrophobic monomer was added into the control agent oligomer chain and reached to their critical chain length, the amphiphilic block copolymer formed micelles by self-assembly in an initial stage of the polymerization. The polymerization then proceeds in the micelles in which well-controlled polymers can be obtained. Thereafter, there are many research works which successfully apply CLRPs in an emulsion polymerization based on self-assembly nucleation such as emulsion ATRP [39, 40], NMP [41-43], RAFT [44-46] and TERP [20, 47-53]. However, these techniques also have some disadvantages such as high temperature of the polymerization for NMP and using a metallic compound of control agents for ATRP and TERP. To our knowledge, there is no any report about ITP in an emulsion polymerization system as an emulsifier-free emulsion iodine transfer polymerization (emulsion ITP)

Therefore, in this research, emulsion ITP is studied in the first time for the synthesis of polymethacrylic acid-*block*-polystyrene (PMAA-*b*-PS) particles using polymethacrylic acid-iodide (PMAA-I) as a macro chain transfer agent and emulsifier to control MWD and good colloidal stability of the obtained polymer particles.

## 1.2 Objective of thesis

1.2.1 To compare the preparation of PMAA-I by solution ITP and RTCP using iodoform as a chain transfer agent.

1.2.2 To investigate the preparation of PMAA-*b*-PS particles by emulsion ITP using PMAA-I as a macro chain transfer agent and emulsifier to obtain PMAA-*b*-PS particles having a narrow MWD with a good colloidal stability.

1.2.3 To characterize the obtained polymer particles.

## 1.3 Scope of thesis

1.3.1 Preparation of PMAA-I macro chain transfer agent by solution ITP and RTCP.

1.3.2 Preparation of PMAA-*b*-PS particles by emulsion ITP

1.3.3 Characterization of the obtained polymer in term of conversion, molecular weight and MWD, particle size and size distribution, zeta potential, morphology, and chemical structure.

## 1.4 The concept of thesis

In a general, there are two particle formations in emulsion polymerization which are micellar and homogeneous nucleations. In the case of micellar nucleation, the polymerization takes place in the micelles previously formed by the emulsifier (the concentration higher than its critical micelle concentration) in aqueous medium. It is well-known that most of the conventional control agents of CLRP techniques are insoluble in water. Therefore, they lose activity to control the polymerization because most of them located in the monomer phase and cannot diffuse via water to enter the micelles or polymerizing particles. In the case of homogeneous nucleation, the preparticles or polymerizing particles formed by the self-assembly of oligomeric chains where their chain lengths reached to critical solubility in water. Based on this mechanism, CLRPs can be applied in emulsion polymerization where the macro chain transfer agents of hydrophilic monomer are pre-polymerized as proposed by Gilbert group [37, 38] before dispersed in aqueous medium. The preparticles or polymerizing particles are formed by self-assembly when the macro chain transfer is unable to dissolve in aqueous medium with the addition of a few unit of monomer. The control agent is then anchor in the polymerizing particle where it can represent the activity to control the polymerization. Similarly, in this work, the macro chain transfer agent of PMAA-I will be firstly synthesized by solution ITP compared with solution RTCP. In a general, in ITP system (Scheme 1.1) [21-23] , iodine radical ($I^{\bullet}$) transfer between two polymerizing chains ($P_1^{\bullet}$ and $P_2^{\bullet}$) where exchange rate ($k_{ex}$) is quite low resulting in less control and livingness of the obtained polymer. When catalyst as a germanium iodide ($GeI_4$) is participated in ITP system called RTCP (Scheme 1.2) [25] , it will be the host of iodine radical in place of one side ($P_1$ or $P_2$) of the ITP system. The deactivation rate constant ($k_{deact}$) is much more than that activation rate constant ($k_{act}$) where the rate of termination would be decreased leading to the improvement of the control and livingness of the obtained polymer.

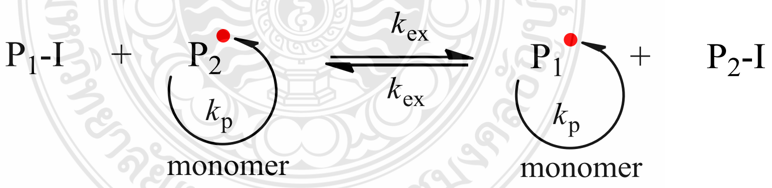
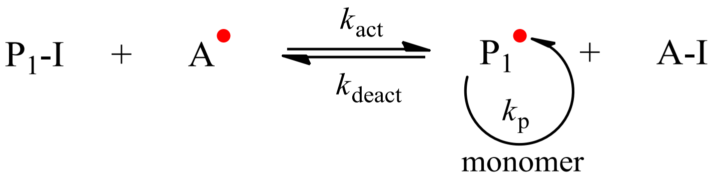


**Figure 1.1** Schematic of Iodine transfer polymerization (ITP) [22]



A = typical element compound
A-I = $GeI_4$ (calalyst)

**Figure 1.2** Schematic of reversible chain transfer catalyzed polymerization (RTCP)[25]

Figure 1.3 shown schematic of self-assembly nucleation in ITP emulsion system expected to occur with using PMAA-I as macro chain transfer agent derived from solution ITP or RTCP and also expected to stabilize polymerizing particles. At the alkaline condition, the carboxyl group of PMAA-I dispersed in aqueous medium would be deprotonated. In early stage of the polymerization, a several units of monomer (styrene; S) will be added to the PMAA-I chain. The hydrophobicity of the polymer chain is increased until reached to the critical chain length. The polymer chains will self-assembly to form the micelle as preparticles. The monomer would be diffused via water to the polymerizing particles. As the present of macro chain transfer agent in the polymer particles, the polymerization would represent a good control and livingness giving polymer with narrow MWD.

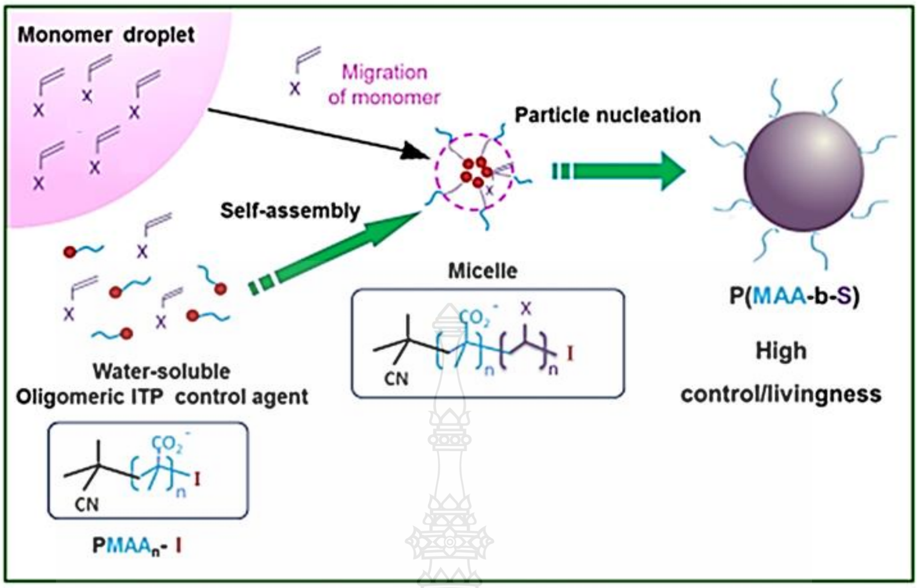


**Figure 1.3** Schematic of self-assembly nucleation in ITP emulsion system

## 1.5 Expectation of thesis

1.5.1 To obtain the optimum conditions for the preparation of PMAA-*b*-PS particles using PMAA-I as a macro chain transfer agent to control MWD of polymer and emulsifier for prevent coagulation.

1.5.2 To obtain a stable PMAA-*b*-PS particles having a narrow MWD.

# CHAPTER 2

# DOCUMENTS AND LITERATURE

## 2.1 Radical polymerization

Polymers can be prepared with various techniques. The most famous are step-growth and chain-growth polymerizations. In step-growth, multifunctional monomers react to give dimers, which then combine with other dimers, trimmers, or other oligomers. At the beginning of the reaction, functional groups of monomers react together to immediately generate a large amount of chains with a low degree of polymerization. As the reaction proceeds, these short chains combine to create longer chains, and the process continues until high molecular weight [54]. The chain-growth mechanism mainly differs in the way that an initiator is used to produce an active site, which can be a radical, cation or anion. When monomer is added one to the active site of polymer chains, the reactive center will transfer to the new unit to renew the active site and continue the propagation. This results in a high molecular weight at even low conversion of monomer [5, 54].

Among active sites in chain-growth mechanism, radical polymerization is the most famous mechanism which was often used in both industry and academic because it is tolerance in both solvent and monomer, compatible with water, low cost and relatively simple [6]. Radical polymerization is consisted of three main reactions as initiation, propagation, and termination. In initiation reaction, an initiator is used to produce radical in which it reacts with first monomer containing unsaturated carbon-carbon bond resulting in the formation of monomeric radical (active center) which then initiate the polymerization. In the propagation step, the obtained monomeric radical rapidly reacts with larger number of monomers. Finally, growing polymer chains are terminated by the combination or disproportionation of bimolecular radicals. The three stages of the radical polymerization are explained more below.

*Initiation:* The initiation step includes two processes. In the first step, the initiator (I) is decomposed to primary radicals (R•) by homolytic cleavage or chemical reaction depending on nature of initiator. The second step, primary radicals react with the first monomer (M) which attacked to carbon–carbon double bonds of monomers such as styrene and ethylene vinyl chloride leading to the initiation of chain growth as shown below.

$$I \xrightarrow{k_d} 2R^{\bullet} \tag{1}$$

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet} \tag{2}$$

*Propagation:* The propagation step is the successive addition of a monomer to a propagating polymer radical chain (RM•) for the growth of polymer chain:

$$RM^{\bullet} + nM \xrightarrow{k_p} P^{\bullet}_{n+1} \tag{3}$$

The propagation proceeds with the addition of monomer to propagating polymer chain with predominantly head to tail placement (98–99%) over head-to head form (1-2%) [5, 6].

*Termination*: It is the reaction where polymer chain radicals are destroyed by combination (4) or disproportionation (5). Combination reaction is the reaction of two chain radicals to give a single polymer molecule with a twice molecular weight. Disproportionation reaction is one chain radical giving an electron to another chain where both chains become inactive chain. Indeed, throughout the radical polymerization includes initiated, propagated, and terminated steps, the polymerization do not control. This results in various limitations such as low control MWDs, unable to prepare block copolymers and complex architectures [55].

$$P^{\bullet}_n + P^{\bullet}_m \xrightarrow{k_t} P_{n+m} \tag{4}$$

$$P^{\bullet}_n + P^{\bullet}_m \xrightarrow{k_t} P_n + P_m \tag{5}$$

## 2.2 Controlled/living radical polymerization

Radical polymerization is one of the most famous mechanisms of the polymerization which has many benefits and widespread use for synthetic polymer. However, the main drawback of this mechanism is high reactivity of propagating radical leading to bimolecular termination. Thereafter, it is the cause of poor control of molecular weight and MWD and also unable to prepare block copolymer and complex architectures.

For this reason, CLRPs are developed in order to produce complex polymers (e.g. block, graft) with narrow MWD. CLRPs are originated by the work of Otsu and co-workers on the inerter mechanism in 1982 [56] . In general, CLRPs are relied on establishing a dynamic equilibrium between a prevalent amount of dormant species (P-A) that are unable to propagate or terminate and dynamic equilibrium propagating radicals (P•) or active species (Figure 2.1). The sufficient large number of activation-deactivation cycles is a requisite for good controlling of chain length distribution. In the conventional process, all chains are easily terminated while in CLRPs, the terminated chains are significantly reduced in which approximately 1-10% of all chains are obtained as a result of the greater number of growing chains. The remaining chains are dormant species, capable of reactivation, functionalization, and chain extension to form block copolymers. Thus, CLRPs behave as a 'living' system [56, 57].

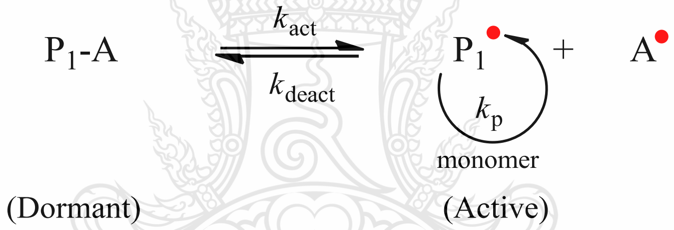
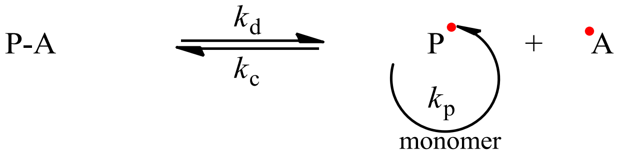


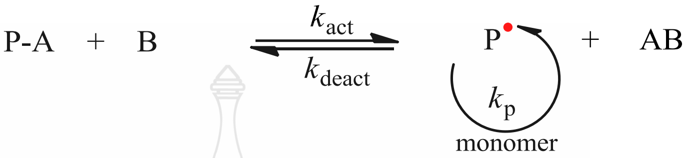
**Figure 2.1** Schematic of general dormant-active equilibrium of CLRP [26]

CLRPs can be divided to two terms as control and livingness. Control refers to number-average molecular weight ($M_n$) increasing linearly with conversion and $M_w/M_n$ decreasing with increasing conversion. Livingness refers to the number fraction of polymer chains in a dormant state which can be chain extended if monomer is available. Currently, the main methods of CLRPs include NMP, ATRP, RAFT, ITP, TERP and RTCP. In a general, the CLRP systems occur via two basic mechanisms relating to the equilibrium between active and dormant spices consisted of the persistent radical effect (PRE) (e.g. NMP and ATRP) and degenerative transfer (DT) (e.g. RAFT, ITP and TERP). In some cases, both PRE and DT may be operative concurrently (e.g. TERP) [29] (Figure 2.2).

(a) Dissociation-Combination (DC)



(b) Atom tranfer (AT)



(c) Degenerlative Chain Transfer (DT)

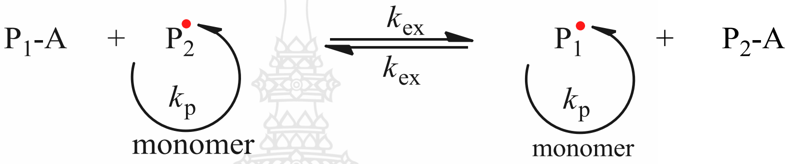


**Figure 2.2** Schematic of the three main mechanisms of activation-deactivation in CLRPs [29]

### 2.2.1 CLRPs based on PRE

The PRE [30, 58-60] can be subdivided as dissociation-combination and atom transfer. The dissociation-combination mechanism is depicted in Figure 2.2 (a) P-A, P•, and A• denote dormant species, propagating radical, and stable free radical, respectively. The term of $k_{act}$ and $k_{deact}$ relate to the rate constants of dissociation $k_d$ (activation) and combination $k_c$ (deactivation), respectively. P–A is thermally or photochemically dissociated giving P• and A•. Normally, P• is consumed by reaction with both P• and A•, but A• is assumed to be stable enough to avoid the reaction with other than the combination with P• and unable to react between themselves including unable to initiate the polymerization. The technique operative with this mechanism is NMP (Figure 2.3 (a)) using nitroxides such as 2, 2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and N-tertbutyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN) as a stable free radical. In the case of atom transfer mechanism (Figure 2.2 (b)), P–A is activated by the transition metal complex as the catalyst (B) to transfer to form a stable species AB• where

A is halogen as Cl and Br. The transition metal complexes as Cu, Fe, Ru, Ni, Os and etc. have been employed as catalysts. These processes are often termed ATRP (Figure 2.3 (b)). The rate constants, $k_a$ and $k_{da}$, are related to $k_{act}$ and $k_{deac}$, respectively.

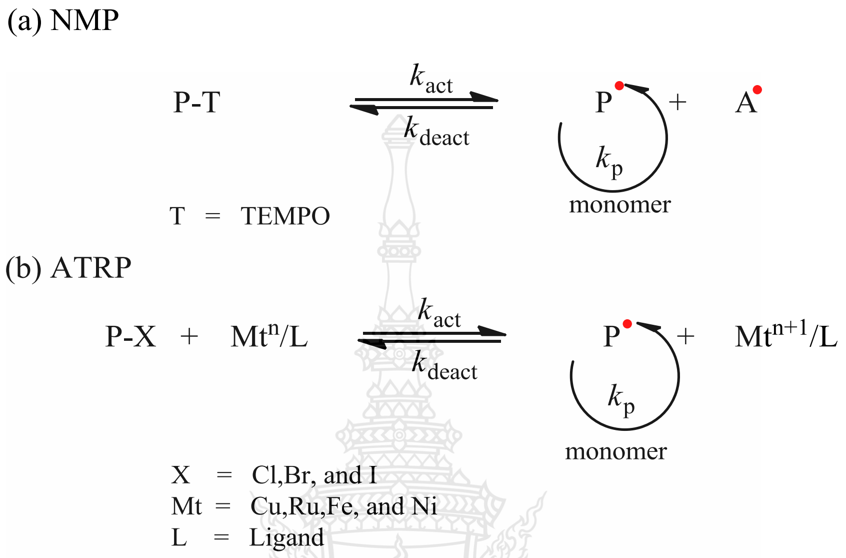
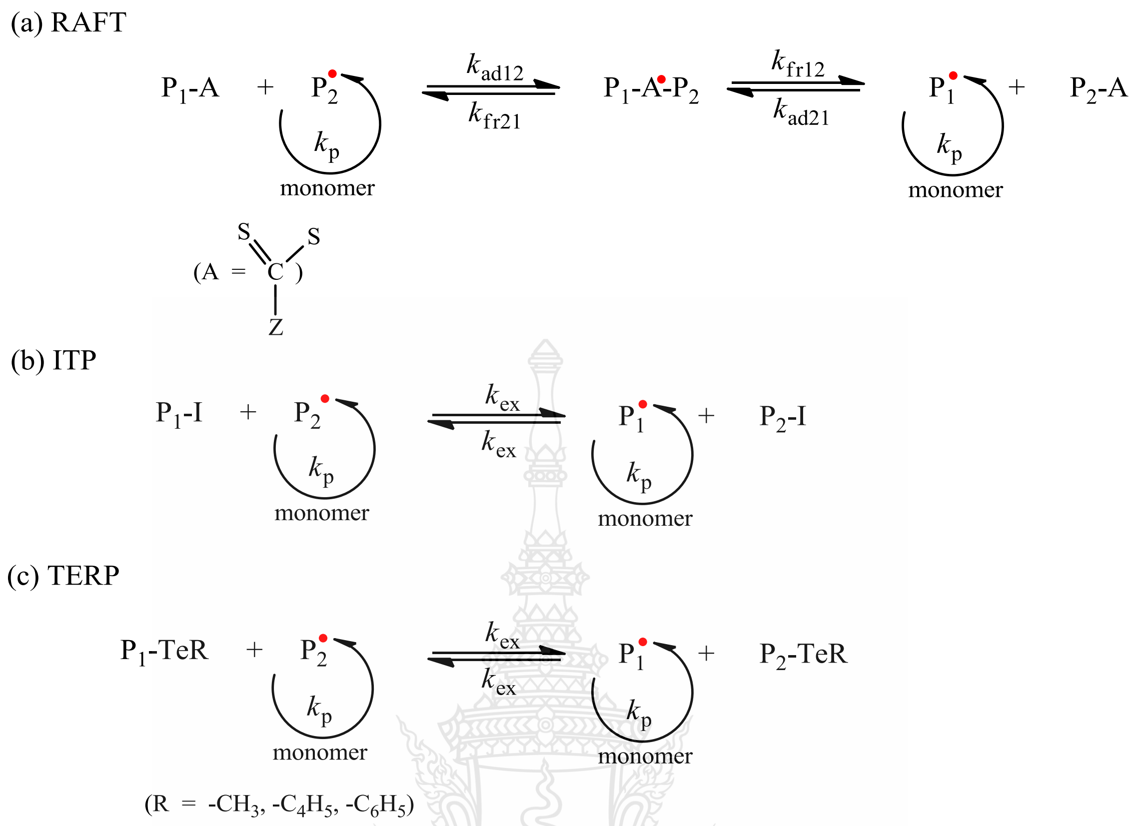


**Figure 2.3** Schematic of CLRPs based on PRE: (a) NMP, (b) ATRP 2.2.2 CLRPs based on DT [29]

### 2.2.2 CLRPs based on DT

CLRPs based on the PRE does not require the addition of a radical initiator because the activation step itself generates a propagating radical [29, 56] .CLRP systems based on DT operate via the interchange of the radical center between active and dormant species by a reversible chain transfer mechanism. In contrast with PRE, DT requires the addition of an initiator to generate the primary radical. In this mechanism, P–A is attacked by the propagating radical (P'•) to form the active species (P•) and the dormant species (P'–A) (Figure 2.2 (c)). This is an exchange reaction of A between two active species (P• and P'•) where A is a chain transfer agent in the form of a diethioesters group, iodine and tellurium compounds in the case of RAFT (Figure 2.4 (a)), ITP (Figure 2.4 (b)), and TERP (Figure 2.4 (c)), respectively.


(a) RAFT

(b) ITP

(c) TERP

**Figure 2.4** Schematic of CLRPs based on DT: RAFT (a), ITP (b) and TERP (c) [29]

## 2.3 Emulsion polymerization

Emulsion polymerization is one of a famous process in heterogeneous system in which the polymerization proceeds via radical polymerization. This process starts with a mixture of initiator (usually water soluble), monomer, emulsifier and water. The prepolymer particles are formed in the aqueous phase via micellar or homogeneous nucleations and swollen by monomer to be the polymerization loci. The polymerization proceeds with the monomer diffusion from monomer droplets to particles in which monomer is consumed in the particles by polymerization. The final product of emulsion polymerization is called latex with polymer particles with a particle size range of 10 to 1000 nm dispersed in aqueous medium [61]. Emulsion polymerization was firstly used for producing synthetic rubbers from butadiene and styrene during World War II for replacing of natural rubber. Thereafter, it grows quickly in an industrial for the commercial polymerization of homopolymers and copolymers of various monomers including vinyl acetate, chloroprene, methacrylates and acrylates. The synthetic latexes prepared by emulsion polymerization can be used directly without further separation. This is the main reason that it can apply to many products including rubbers, paints, plastic, coating, and adhesives. The emulsion polymerization has several advantages over homogeneous polymerization techniques such as using nontoxic and inexpensive continuous phase as water and also faster heat transfer than that of bulk polymerization. In particular, the polymerization rate is much higher than that of homogeneous polymerization due to lower rate of termination. Because the radicals are compartmentalized within particles, they cannot terminate with the other polymeric radical within another particle leading to higher molecular weight [3, 62].

### 2.3.1 General ingredients of emulsion polymerization

The main ingredients in emulsion polymerization consist of four components which are monomer, dispersion medium or continuous phase, emulsifier, and initiator. The description of ingredients are explained below.

#### 2.3.1.1 Monomer

Monomers are an oil phase which normally act as a reservoir to support the polymerization. Many kinds of monomer can be used in emulsion polymerization such as styrene, butadiene, acrylonitrile, acrylate ester and methacrylate ester monomers, vinyl acetate, acrylic acid and methacrylic acid, and vinyl chloride. The distinct of structure and water solubility of monomer are important and influence on a particle formation in emulsion polymerization. The high water solubility monomer is normally polymerized via homogeneous nucleation where the particles are formed without the presence or need of micelles. In contrast, using low water solubility monomers, the particle formation take place in the micelles [1,54, 61-63].

#### 2.3.1.2 Continuous phase

The continuous phase in an emulsion polymerization is usually water (deionized water is most typically used) due to low viscosity, inexpensive and environmentally friendly. Moreover, it presents excellent ability to heat transfer which enables fast polymerization rates with preventing auto-acceleration. The duty of continuous phase is the medium for the solubility of initiator, emulsifier and other ingredients. Moreover, it is the loci of particle formation and the transfer of monomer from droplets to particles [1, 54, 61-63].

### 2.3.1.3 Emulsifiers

An emulsifier or surfactant is amphiphilic molecule used to stabilize monomer droplets and polymer particles by preventing aggregation. If the concentration of emulsifiers exceed their critical micelle concentration (CMC), they aggregate to form micelles (approximately 2-10 nm in diameter) and become the loci of polymerization. Usually, they can be classified to three main groups as anionic, cationic and non-ionic emulsifiers. Anionic emulsifiers are the most commonly used in emulsion polymerization such as prominent alkyl sulfates include ammonium lauryl sulfate, sodium lauryl sulfate (or sodium dodecyl sulfate), and the related alkyl-ether sulfates sodium laureth sulfate (or sodium lauryl ether sulfate). They normally provide a negative charge as sulfate, sulfonate, phosphate and carboxylates on their hydrophilic chain ends. This charge prevents polymer particle aggregation by electrostatic repulsion. Cationic emulsifiers as the salts of long chain amines, polyamines, and quaternary ammonium salts behave similar to anionic surfactant to stabilize the particle using the positive charge. Finally, Nonionic emulsifiers such as poly(ethylene oxide), poly (vinyl alcohol) and hydroxyethyl cellulose are sometimes used in conduction with anionic emulsifiers for improving the freeze-thaw and shear stability of the polymer or to aid in controlling particle size and size distribution. Nonionic emulsifiers stabilize the polymer particles with steric repulsion using long hydrophilic segment. Non-ionic emulsifiers are also used to improve the stability of the final polymer latex against wide range of ph. In some cases, nonionic emulsifiers were used to co-stabilize with ionic emulsifiers because their efficiency in producing stable emulsions is less than those of both anionic and cationic emulsifiers. Emulsifiers increase particle number and decrease particle size as their concentrations in the initial reaction charge are increased. However, one can use to improve particle stability, without affecting the particle number, size and size distribution by post addition of emulsifier after nucleation is complete [1, 54, 61-63].

### 2.3.1.4 Initiators

The initiators used in emulsion polymerization are usually water-soluble initiators such as potassium or ammonium per sulfate, hydrogen peroxide, and 2, 2-azobis (2-amidinopropane) dihydrochloride. Partially water-soluble peroxides such as succinic acid peroxide and t-butyl hydroperoxide and azo compounds such as 4, 4-azobis (4-cyanopentanoic acid) have also been used. Redox systems such as per sulfate with ferrous ion are commonly used. They are advantageous in yielding desirable initiation rates at temperatures below 50 °C. Other useful redox systems include cumyl hydroperoxide or hydrogen peroxide with ferrous, sulfite, or bisulfite ion [1, 54, 61-63].

### 2.3.2 Mechanism of particle nucleation in emulsion polymerization

In general, radical polymerization is mainly used in emulsion polymerization. Normally, this mechanism is divided to three steps as initiation, propagation and termination. It is known that polymerization loci of emulsion polymerization are polymer particles which formed by either homogeneous or micellar nucleation. Homogeneous nucleation is the formation of particle nuclei in the aqueous phase when the continuous phase contains low concentration or without emulsifier. In polymerization process, monomer firstly mixed with the aqueous phase at mild stirring rate to give the large portion of monomer as the monomer layer floating on the aqueous phase containing the small portion of monomer. When initiator is added into aqueous phase and created primary radicals, they then are reacted with monomers soluble therein to be oligomer or growing chains. The growing chains are insoluble in aqueous medium when their chain lengths reach to the critical water solubility ($J_{\text{critical}}$) leading to the formation of preparticles or precursors. The preparticles are formed by self-assembly using hydrophilic part from water-soluble initiator as outwards part for preventing the coagulation of polymer particles while hydrophobic unit part derived from monomer molecules is inward as shown in Figure 2.5. Thereafter, growing precursor particles are swollen by monomer diffused from monomer droplets and polymerized there until the consumption of monomer. The obtained polymer particle size is in the range of 300-600 nm with low relatively colloidal stability. Due to lower polymerization rate compared with micellar nucleation, it normally does not used in industry.

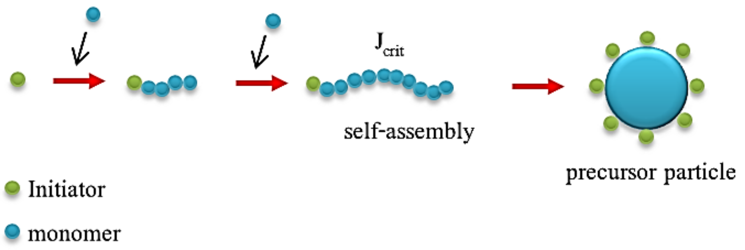


**Figure 2.5** Schematic of Homogeneous nucleation [64]

In the case of micellar nucleation as shown in Figure 2.6, preparticles are formed in the micelles when the concentration of emulsifier over its CMC where the micelles form using the hydrophilic and hydrophobic as outwards and inwards part, respectively. Due to the hydrophobic part inside micelles, they are swollen by monomer. After primary radicals produced by initiator are dissolved in aqueous phase and react with monomer, the growing oligomer chains become more hydrophobic than hydrophilic called surface active. They then enter to the monomer-swollen micelles and continue to propagate by reacting with monomers therein. The monomer-swollen micelles containing oligomeric radicals are called precursor particles. The preparticle dispersed in the aqueous phase continue to grow with the polymerization therein where monomer is supported by the diffusion of monomer from monomer droplets until the monomer depletion similar to homogeneous nucleation mechanism [65-69].

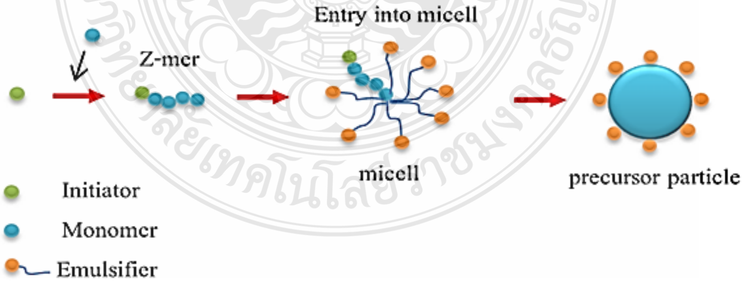


**Figure 2.6** Schematic of Micellar nucleation [64]

### 2.3.3 Theory proposed by Hawkins and Smith and Ewart

Smith and Ewart [63] and Harkins [70] develops the first successful theory to explain the distinct features of emulsion polymerization of polystyrene in the 1940s. Smith and Ewart arbitrarily divided the mechanism of emulsion polymerization into three stages or intervals. However, it has been recognized that not all monomers or systems undergo these particular three intervals (Figure 2.7). Nevertheless, based on their descriptions, it is a useful starting point to analyze the kinetic of emulsion polymerization at least the particle formation by micellar nucleation. Interval I is the formation of the preparticles where the oligomer chain radicals enter in monomer-swollen micelles until the disappearance of free micelles. In this step, monomer conversion is normally about 20%. In addition, the number of particles continuously enlarges througout this step leading to the increase of polymerization rate. The interval II, polymerization specifically occur inside the polymer particles by diffusion of monomer from monomer droplets via aqueous medium into the polymerizing particles to maintain the monomer concentration therein in which the rate of polymerization is constant. The size of polymer particles increases until the disappearence of monomer droplets as the finish of the interval II (50-90% conversion). In the interval III, the polymerization continues within polymer particles until all monomer remained in particles has been consumed. In a general, the rate of polymerization gradually decreased with monomer concentration.

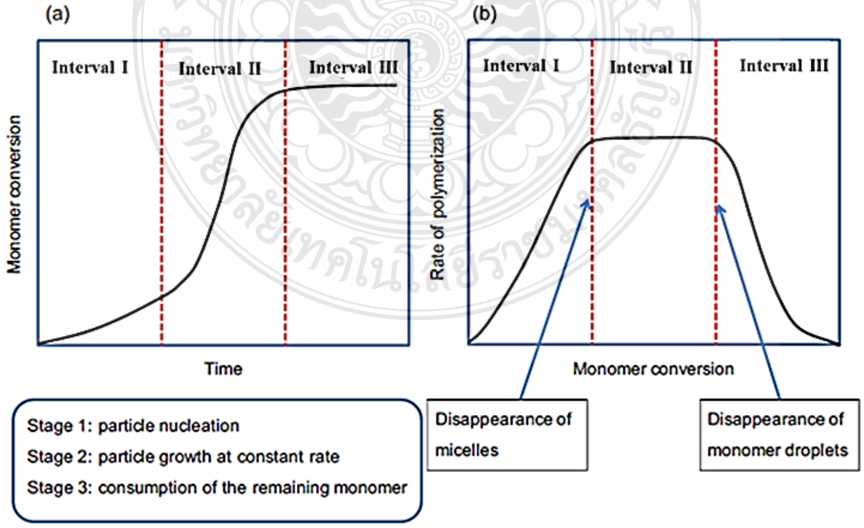


**Figure 2.7** Schematic of the classification occurs in the synthetic emulsion [69]

The limit of Smith-Ewart theory is that it does not predict the specific polymerization behavior when the monomer is somewhat water-soluble liked methyl methacrylate or vinyl acetate. In these cases, homogeneous nucleation preferably occurs [69, 71, 72].

## 2.4 CLRP in emulsion polymerization

In an ab initio emulsion polymerization [62, 69], the reaction system initially starts with a stirred mixture of water as continuous phase, water soluble initiator, monomer, and emulsifier or surfactant where monomer droplets and micelles are formed and dispersed in a continuous aqueous phase. Thereafter, initiator radicals are generated in the aqueous medium to form polymer particles swollen with monomers dispersing in an aqueous medium via micellar or homogeneous (case of surfactant-free emulsion polymerization) nucleation to be the polymerization locus. Monomer droplets only work as reservoir to supply monomer to the polymerizing particles via the aqueous medium. Therefore, it is difficult for hydrophobic control agents, which are pre-soluble in monomer phase, to diffuse via water into polymerizing particle and coexist with propagating radicals therein. To overcome this drawback, Hawkett and coworkers [31, 37 and 38] proposed a clever idea in emulsion RAFT polymerization of n-butyl acrylate (BA) or styrene with water-soluble polyacrylic acid (PAA) oligomer RAFT reagent, which was named self-assembly nucleation. In emulsion RAFT polymerization, a water-soluble PAA oligomer radical [38], which is formed by the reaction of the water-soluble PAA oligomer RAFT reagents with initiator radical, adds to hydrophobic monomers dissolved in the aqueous medium to form amphiphilic block oligomer. When the hydrophobic block chain reaches to a critical chain length, at which the hydrophobic block chain precipitates in water, they form micelles by self-assembly. The micelles then are swollen with monomer and the polymerization takes place therein by the entering of initiator radicals from an aqueous medium like a general emulsion polymerization with emulsifier (Figure 2.8). Thereafter, based on the same idea, the other groups successfully applied it in RAFT [44-46] and NMP [41-43] systems.

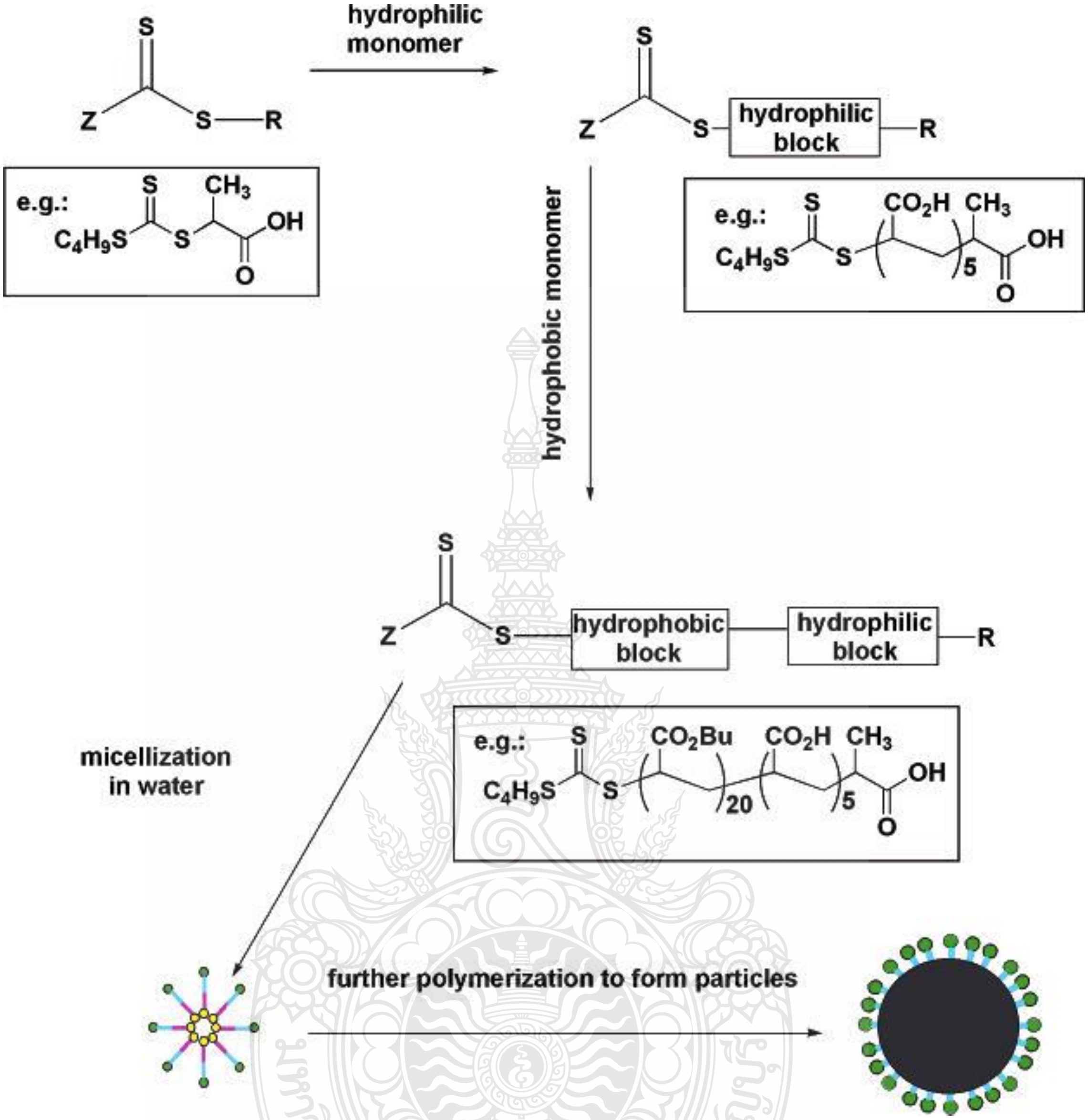


**Figure 2.8** Schematic of RAFT *ab initio* emulsion polymerization via Self-Assembly [37].

For emulsion RAFT polymerization, Yeonhwa Wi and coworks [73] studied *ab initio* batch emulsion polymerization of styrene using anionic chain transfer agent as poly(methacrylic acid) (PMAA) macro-RAFT agent. The stable PS emulsion was obtained. In addition, size of PS particle reduced with the increase of the macro-RAFT agent amount. The results indicate that the PMAA macro-RAFT agent represented high efficiency to form block copolymer P(S-b-MAA) with high control and livingness. The later process has been conculded that tritaiocarbornate RAFT agent give better control over the MWD than dibiobenzoate RAFT. (although both systems typically give good colloidal stability). The macro-RAFT agent needs to be sufficiently hydrophobic for micellar nucleation to dominate; otherwise, particles may form mainly via homogeneous nucleation [74]. Moreover, Rieger, Jutta and et al implemented to use nonionic chain transfer agent as poly(ethylene oxide)-based trithiocarbonate (PEO-TTC) RAFT in the *ab initio* emulsion RAFT of styrene and n-butyl acrylate at 80 °C (Figure 2.9) [45, 75]. In addition, PEO-TTC RAFT chain transfer agent exhibited very good agreement $M_n$ between experiment and the theoretical values with low $M_w/M_n$ as showed in Figure 2.10 [75].

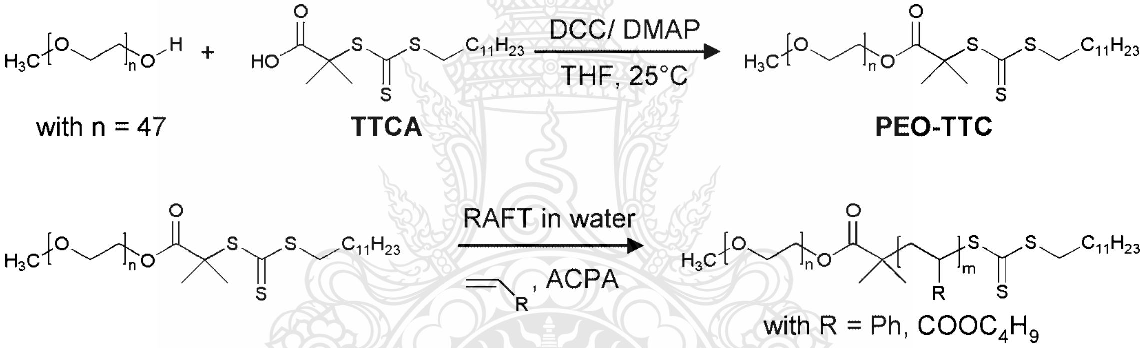


**Figure 2.9** Schematic of synthetic route for emulsion RAFT polymerization of styrene and n-butyl acrylate [45]

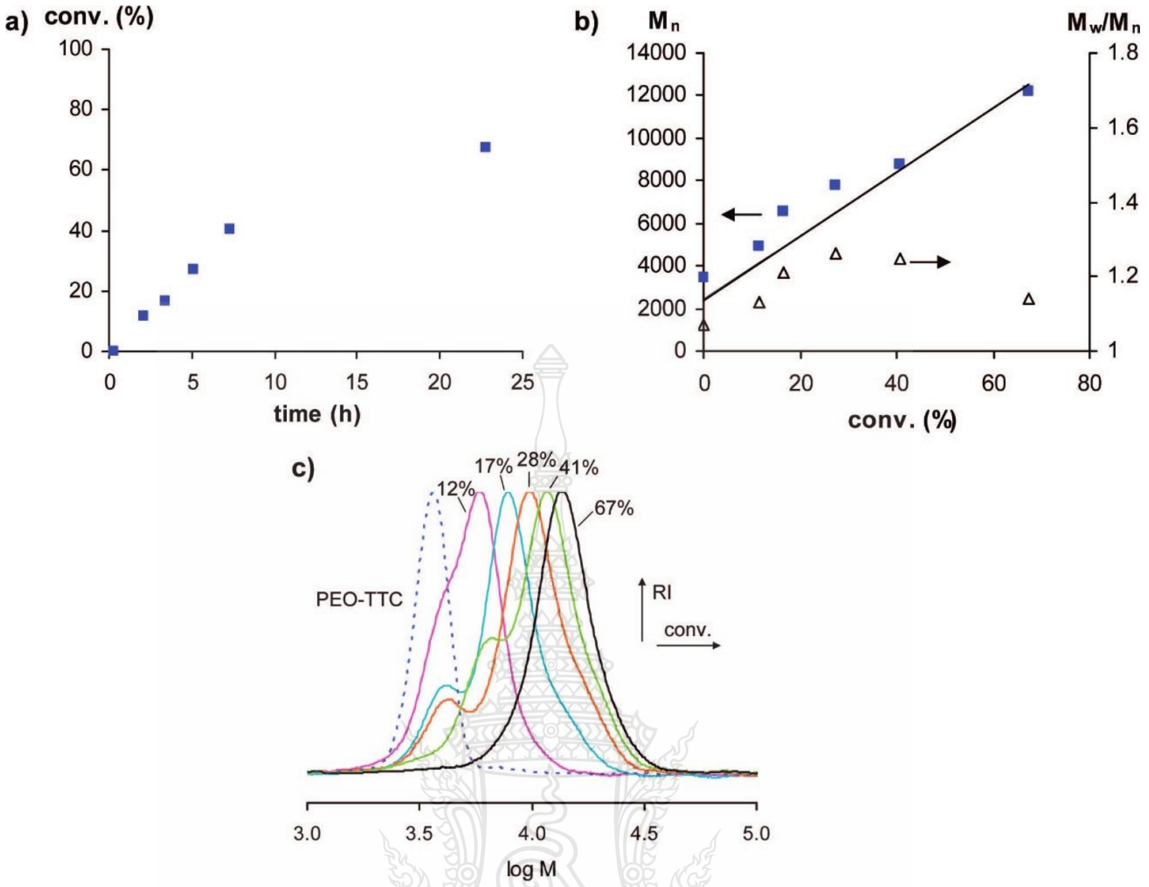


**Figure 2.10** Emulsion RAFT polymerization of styrene using the poly(ethylene oxide) based trithiocarbonate (PEO-TTC)RAFT agent at 80 °C: (a) monomer conversion determined bygravimetry vs time; (b) number average molar mass, $M_n$, andpolydispersity index, $M_w/M_n$, determined by size exclusionchromatography (polystyrene calibration) vs conversion; the straight line corresponds to the theoretical $M_n$ vs conversion;(c) evolution of size exclusion chromatograms with conversion [75]

For emulsion NMP, Charleux and co-workers [76] have successfully polymerized n-butyl acrylate (BA) and styrene using water-soluble macro initiator of poly(acrylic acid) SG1-based macro-alkoxyamine (PAA–SG1) in alkaline water at 120 °C. The macroinitiator eventually become the surfactant to stabilize particle by PAA segment where the spherical particles were obtained with a diameter generally less than 100 nm with narrow particle size distribution. In addition, the average particle diameter of poly(n-butyl acrylate) was systematically larger than that of polystyrene (Figure 2.11).

In addition, alkoxyamine macroinitiators based on methacrylic acid as water-soluble SG1 nitroxide-capped poly(methacrylic acid-co-styrene) macroalkoxyamines ((PMAA-co-PS)-SG1) was used as initiators for methyl methacrylate (MMA) polymerization in alkaline conditions at temperatures below 90 °C [77]. The polymerization was well-controlled polymer chains and led to low-polydispersity. Similaly, Thomson et al. [43] accompanied SG1-mediated emulsion polymerization of n-BMA with 10 mol % styrene, in both the presence and absence of surfactant, yielded well-controlled polymerizations.

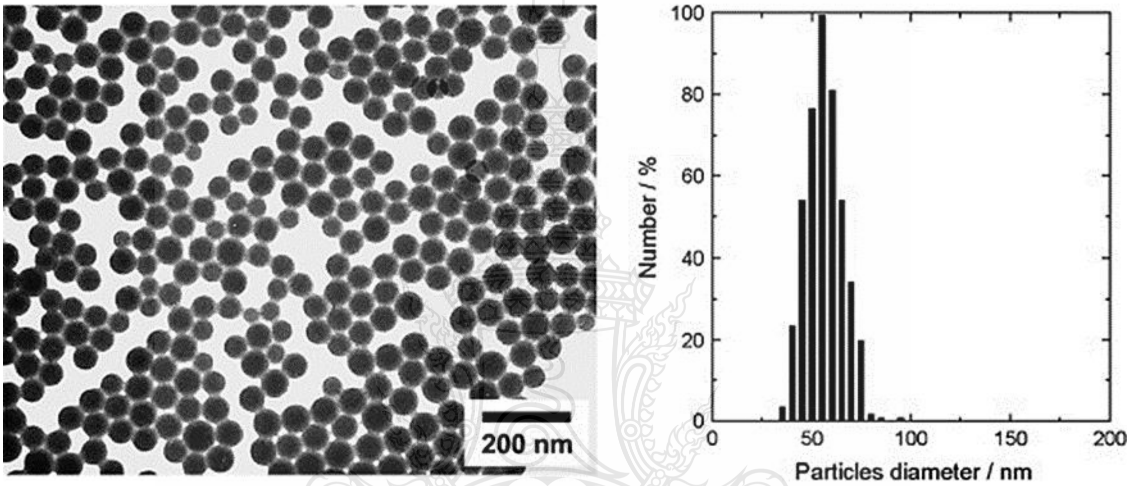


**Figure 2.11** Particle size distribution and TEM photograph of PS particles obtained by SG1-mediated *ab initio* emulsion NMP employing a SG1-terminated poly(sodium acrylate) macroinitiator at 120 °C [76]

In addition, the self-assembly technique has also been applied in emulsion TERP of BA or styrene using poly(methacrylic acid) (PMAA; degree of polymerization: 30)-methyltellanyl (TeMe) ($PMAA_{30}$-TeMe) as a control agent [20, 47-53], in which PMAA block was used in place of PAA block to avoid back biting reaction [78, 79]. It was reported that emulsion TERP of styrene at 60˚ C, resulting in good livingness and the number-average molecular weight linearly increased with the conversion. However, polymer particles had bimodal size distributions comprising submicrometer-sized and nanometer-sized particles. Nevertheless, the particle formation mechanism was uncertain [80]. After carefully study, it was found that the temperature affects the particle formation.

The sizes of the obtained PS particles are nanometer-sized particles at 50˚ C, submicrometer-sized ones at 70˚C and both particles at 60˚C were obtained. There are two possible particle formation mechanisms in the emulsion TERP [48] as a fallow (Figure 2.12): (i) Self-assembly nucleation: (ii) Homogeneous nucleation. Amphiphilic block copolymers formed in the early stage of the polymerization and become micelles, which works polymerization loci, resulting in a stable nanometer-sized PS particle due to the ionized sodium $PMAA_{30}$ block. Homogeneous nucleation is also known in emulsifier-free emulsion polymerization. Ionized initiator radicals derived from V-501 react with monomers dissolving in an aqueous phase up to a certain critical degree of polymerization and then precipitate in the aqueous phase, eventually resulting in the formation of primary particles. Because the primary particles do not have $PMAA_{30}$ hairy layer at the surface, they further combined each other, resulting in the submicrometer-sized particles. From these results, it is concluded that the particle formation by self-assembly nucleation in the early stage of the emulsion TERP is important for the formation of the monomodal nanometer-sized PS particles with good control/livingness. Therefore, minimization of homogeneous nucleation can be achieved at low temperature (at 50 °C) [49] and high stirring rate [81] before increase the temperature (over 70°C) to reduce the polymerization time after the first stage of polymerization. The total surface area of the preparticles is high enough to avoid the secondary particle formation by homogeneous nucleation where most of oligomer zing chains (at surface active or z-mer) initiated in aqueous media enter to the preparticles before reaching the $J_{crit}$ chain length.

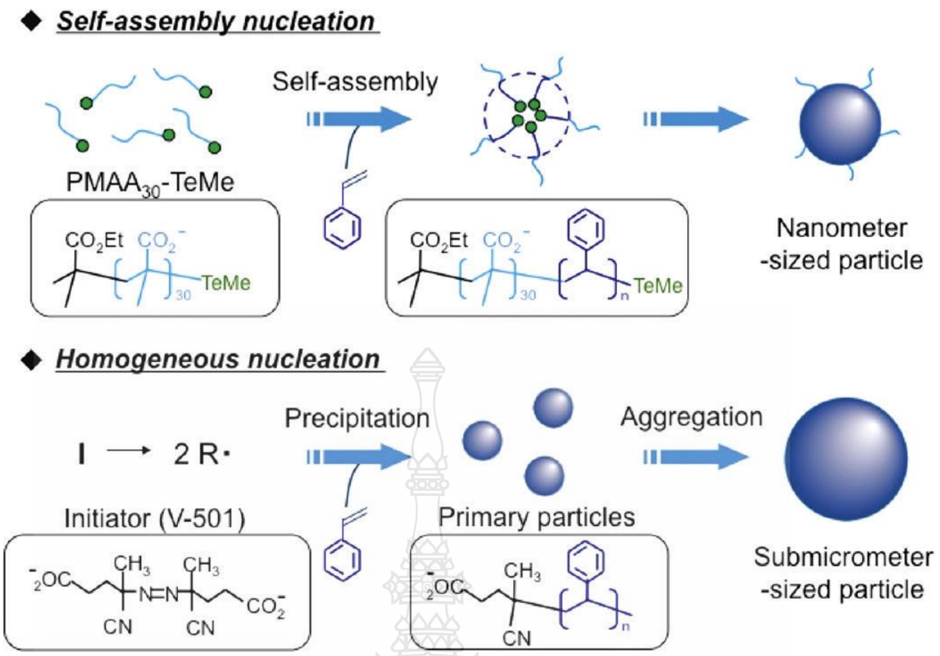


**Figure 2.12** Particle Formation Mechanisms in the Emulsion TERP of Styrene: (i) Self Assembly Nucleation; (ii) Homogeneous Nucleation [48]

However, based on the drawback of emulsion NMP, emulsion ATRP and emulsion TERP as mentioned above and to our knowledge, there is no any report about emulsion ITP. Therefore, it is interesting in order to investigate those techniques to prepare a stable polymer emulsion.

# CHAPTER 3
# EXPERIMENTAL PART

## 3.1 Chemicals and instruments

### 3.1.1 Chemicals

| Name | Brand | Model |
|---|---|---|
| 1. Methacrylic acid (MAA) | Analytical Reagent | Sigma-aldrich |
| 2. Styrene (S) | Reagent Plus | Sigma-aldrich |
| 3. Iodoform ($CHI_3$) | Analytical Reagent | Sigma-aldrich |
| 4. Germanium (IV) iodide | Analytical Reagent | Sigma-aldrich |
| 5. Hydroquinone | Analytical Reagent | Sigma-aldrich |
| 6. 2, 2'-Azobis(4-methoxy-2, 4-dimethylvaleronitrile) (V-70) | Analytical Reagent | Wako |
| 7. 4, 4'-Azobis(4-cyanopentanoic acid) (V-501) | Analytical Reagent | Wako |
| 8. Potassium hydroxide (KOH) | Analytical Reagent | Univar |
| 9.Trimethylsilyldiazomethane (TMSD) | 2 M in hexane | Across |
| 10. Methanol | Analytical Reagent | RCI labscan |
| 11. Acetic acid | Analytical Reagent | RCI labscan |
| 12. Dioxane | Analytical Reagent | RCI labscan |
| 13. Dimethylformamide (DMF) | Analytical Reagent | RCI labscan |
| 14. Tetrahydrofuran (THF) | Analytical Reagent | RCI labscan |
| 15. Diethyl ether | Analytical Reagent | RCI labscan |
| 16. Deuterated chloroform ($CDCl_3$) | Analytical Reagent | Sigma-aldrich |

### 3.1.2 Apparatus

| Name | Model | Brand |
|---|---|---|
| 1. Dynamic light scattering (DLS) | Delsa nano C | Beckman |
| 2. Transmittance electron microscope (TEM) | Tecni20 G2 | Phillips |
| 3. Scanning electron microscope (SEM) | JSM5610 | JEOL |
| 4. Atomic Force Microscopes (AFM) | - | Bruker |
| 5. Proton ($^1$H) and diffusion order spectroscopy (DOSY) NMR | Advanced AM400 | Bruker |
| 6. Gel permeation chromatography (GPC) | Water 2414 | Water |
| 7. pH meter | 4831 | Consort |

## 3.2 Experimental Plan

3.2.1 Synthesis of PMAA-I by solution ITP and RTCP.

3.2.2 Synthesis of PMAA-*b*-PS particles by emulsion ITP using PMAA-I as a macro chain transfer agent.

3.2.2.1 Study of the influence of the continuous phase pH at acidic (uncontrol pH) and alkaline (control pH) conditions.

3.2.2.2 Study of the influence of the utilization of PMAA-I with and without the purification as a macro chain transfer agent.

3.2.2.3 Study of the influence of the post addition of $CHI_3$ after polymerization at various times in emulsion ITP using purified PMAA-I.

3.2.2.4 Study of the influence of additional amount of $CHI_3$ in emulsion ITP using purified PMAA-I on the control manner of the obtained PMAA-*b*-PS.

## 3.3 Experimental and characterization

In this research, the preparation of PMAA-*b*-PS particles was divided into two steps. The first step, PMAA-I was prepared by solution ITP and RTCP to compared for using as a macro chain transfer agent in the emulsion ITP. The second step, The PMAA-*b*-PS particles were prepared by emulsion ITP.

### 3.3.1 Synthesis of PMAA-I by solution ITP and RTCP polymerization

PMAA-I was prepared by solution polymerization using iodoform as a chain transfer agent (germanium iodide as a catalyst for RTCP) as follow. Firstly, MAA and $CHI_3$ were dissolved in dioxane and added into a round-bottom Schlenck flask (the cased of solution RTCP, $GeI_4$ was also added as a catalyst). The flask was closed off with a silicone rubber septum degassed using several nitrogen gas/vacuum cycles (finally in nitrogen condition). It was then immerged in an oil bath at 40 °C. After that, V-70 as an initiator dissolved in dioxane was injected via syringe into the round-bottom Schlenk flask to start the polymerization with magnetic stirrer at stirring rate of 500 rpm for 24 h. The schematic diagram of the synthesis of PMAA-I and condition used were shown in Fig 3.1 and Table 3.1, respectively. In the case of using purified PMAA-I will be conducted as follows. The obtained PMAA-I solution was purified by precipitation in diethyl ether, filtered and dried in a vacuum oven at room temperature. Both PMAA-I with and without (PMAA-I solution) purification were used as a macro chain transfer agent and stabilizer in the further emulsion polymerization. The %conversion, weight- and number-average molecular weights ($M_w$ and $M_n$, respectively) and chemical structure of PMAA-I were characterized.

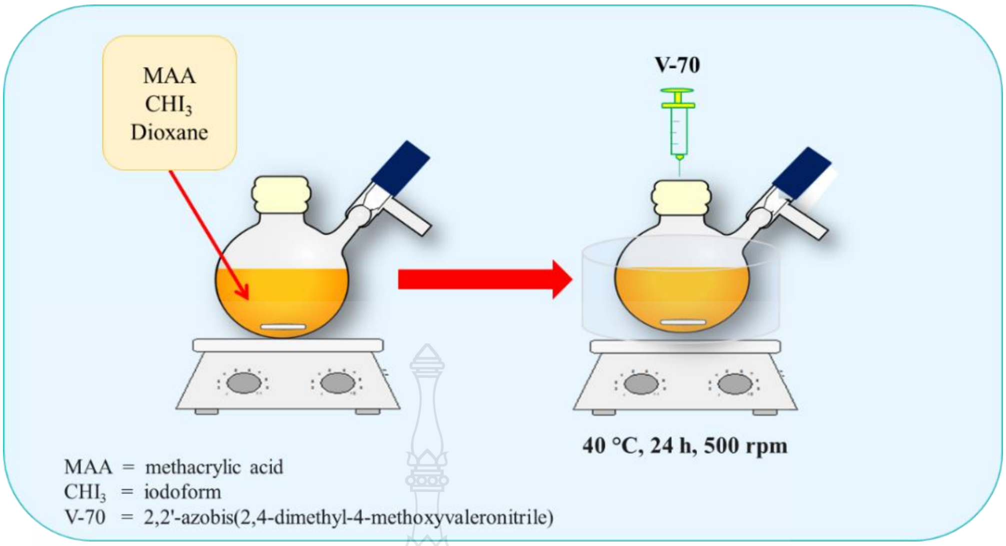


**Figure 3.1** Schematic diagram for the preparation of PMAA-I by solution ITP

**Table 3.1** Reagent amounts for the synthesis of PMAA-I as a macro chain transfer agent by solution ITP[a] and RTCP[a] with $CHI_3$ as a chain transfer agent and V-70 as a initiator

| Ingredients | | Methods | |
|---|---|---|---|
| | | Emulsion ITP | Emulsion RTCP |
| MAA | g (mmole) | 6.5 (75.0) | 6.5 (75.0) |
| $CHI_3$ | g (mmole) | 2.0 (5.0) | 2.0 (5.0) |
| Gel$_4$ | mg (µmole) | - | 22.0 (38.0) |
| V-70 | g (mmole) | 1.2 (3.7) | 1.2 (3.7) |
| Dioxane | g | 35.0 | 35.0 |

[a] $[MAA]_0/[CHI_3]_0$ = 15/1 molar ratio

$[MAA]_0/[V\text{-}70]_0$ = 20/1 molar ratio

$[CHI_3]_0/[V\text{-}70]_0$ : = 1.35/1 molar ratio

40 °C, 24 h, $N_2$, 500 rpm.

### 3.3.2 Synthesis of PMAA-*b*-PS by emulsion ITP using PMAA-I as macro chain transfer agent

The procedure of emulsion ITP is described below. Firstly, aqueous solution was added into a round bottom Schlenk flask. The flask was closed off with a silicone rubber septum before being degassed using several nitrogen gas/vacuum cycles (finally in nitrogen gas condition). Secondary, PMAA-I dioxane solution, and styrene were respectively injected via syringe into a round-bottom Schlenk flask. In the case of using purified PMAA-I was added since first step. The flask was then placed in an oil bath at 60 °C with stirring rate of 500 rpm. Finally, V-501 as an initiator dissolved in aqueous solution, was injected via syringe into the flask to start the polymerization. The schematic diagram for synthesis of PMAA-*b*-PS particles by emulsion ITP was shown in Fig 3.2. The influences of various parameters on preparation of polymer particles were investigated.

3.3.2.1 Influence of the continuous phase pH at acidic (unadjusted pH) and alkaline (adjust pH with 1 M KOH) were studied. The condition listed is shown in table 3.2.

3.3.3.2 Influence of the utilization of PMAA-I with and without the purification as a macro chain transfer agent was investigated using the condition listed in same as in Table 3.2 at alkaline condition.

3.3.3.3 Influence of the post addition of $CHI_3$ after polymerization at various at 90, 60 and 30 mins in emulsion ITP using purified PMAA-I were studied using the condition in Table 3.3.

3.3.3.4 Influence of additional amount of $CHI_3$ in emulsion ITP using purified PMAA-I on the control manner of the obtained PMAA-*b*-PS were studied. The condition is shown same as in Table 3.3 with various amount of $CHI_3$
(0.43 to 0.86 and 1.71 mmol).

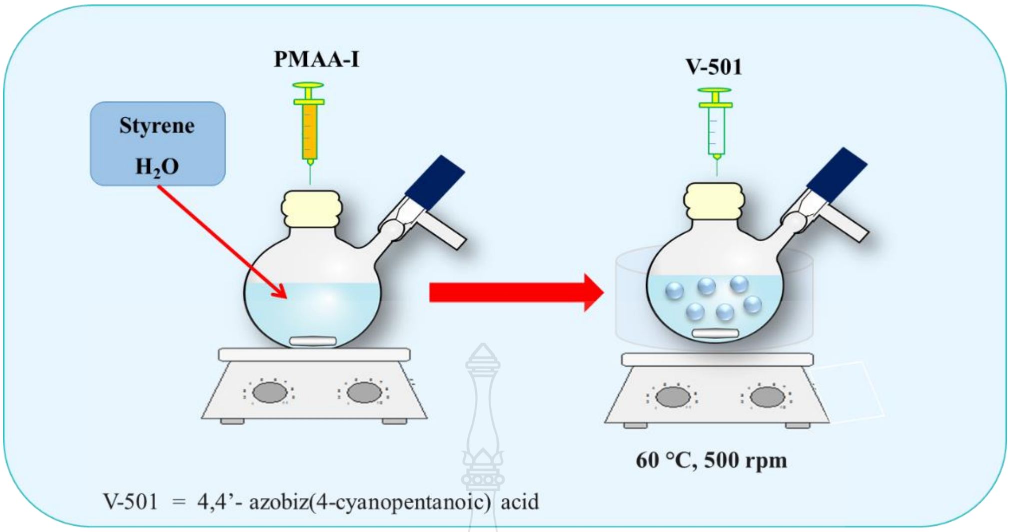


**Figure 3.2** Schematic diagram for the preparation of PMAA-*b*-PS particles by emulsion ITP

**Table 3.2** Recipe for the synthesis of PMAA-*b*-PS by emulsion ITP[a] of styrene using PMAA-I as a macro chain transfer agent and V-501 as an initiator at acidic (pH~4) alkaline (pH~9)[b]

| **Ingredient** | | |
|---|---|---|
| Styrene | g (mmol) | 10.4 (100.0) |
| PMAA-I[c] | mg (µmol) | 950.0 (250.0) |
| V-501 | mg (µmol) | 70.0 (250.0) |
| Water | g (mmol) | 90.0 |

[a] $[\text{Styrene}]_0/[\text{PMAA-I}]_0 = 400/1$, molar ratio.

$[\text{Styrene}]_0/[\text{V-501}]_0 = 400/1$, molar ratio.

$[\text{V-501}]_0/[\text{PMAA-I}]_0 = 1/1$, molar ratio.

60 °C, $N_2$, 500 rpm.

[b] Adjusted pH with 1 M KOH solution.

[c] Added a PMAA-I dioxane solution 6.5 g (without purification) with $M_n$ of PMAA-I as 3781 g/mol.

**Table 3.3** Recipe for the synthesis of PMAA-*b*-PS by emulsion ITP[a] of styrene using PMAA-I (with purification) as a macro chain transfer agent and V-501 as an initiator at alkaline (pH~9)[b] with adding of $CHI_3$ solution[c] after polymerization

| **Ingredient** | | |
|---|---|---|
| Styrene | g (mmol) | 10.4 (100.0) |
| PMAA-I[d] | mg (μmol) | 720.0 (250.0) |
| V-501 | mg (μmol) | 70.0 (250.0) |
| $CHI_3$ | mg (mmol) | 168.5 (0.43) |
| Water | g (mmol) | 90.0 |

[a] $[\text{Styrene}]_0/[\text{PMAA-I}]_0 = 400/1$, molar ratio
$[\text{Styrene}]_0/[\text{V-501}]_0 = 400/1$, molar ratio
$[\text{V-501}]_0/[\text{PMAA-I}]_0 = 1/1$, molar ratio
60 °C, $N_2$, 500 rpm

[b] Adjusted pH with 1 M KOH solution

[c] $CHI_3$ soluble in 5 ml of dioxane

[d] Added a PMAA-I with $M_n$ of PMAA-I as 2879 g/mol

### 3.3.3 Characterizations of PMAA-I and PMAA-*b*-PS particles

#### 3.3.3.1 % Conversion measurement

% Conversion was measured by gravimetry. Firstly, PMAA-I solution and PMAA-*b*-PS emulsion (~2.0 g) were taken from the reactor and transferred directly into aluminum cup and weighted. Several drops of hydroquinone solution (1 wt%) were added therein to stop polymerization reaction before the free liquid was evaporated in an oven at 70℃. The sample was dried until a constant weight of the dried polymer was obtained. Monomer conversion was obtained by comparing the weight of dried polymer with that of the original monomer as the equation 3.1

$$\%\ \text{Conversion} \quad = \quad \frac{\text{Mass of dried polymer}}{\text{Mass of monomer}} \times 100 \qquad (3.1)$$

3.3.4.2 Molecular weight measurement

$M_w$, $M_n$ and MWD of PMAA-I and PMAA-*b*-PS obtained were measured by GPC. Before measurement, the carboxyl groups of MAA unit in PMAA-I and PMAA-*b*-PS were derivatives by TMSD to be methyl ester groups where PMAA-I finally changed the form to be polymethyl methacrylate iodide (PMMA-I) [32]. The dried PMAA-I sample(~0.1 g) was dissolved in solvent mixture of methanol/DMF (2/8 wt).Thereafter, 0.5 g of TMSD solution (2M in hexane) was added drop wise into the polymer solution, in which the reaction was allowed to continue overnight at room temperature. After excess TMSD was destroyed by 0.2 g of acetic acid, the methylated polymer solution was precipitated by drop wise addition into 15 ml of methanol. In the final, the precipitated PMMA-I was then filtrated and dried. The accurate weight of dried methylated polymer was completely dissolved in THF in order to obtain the polymer concentration of 1 wt% before GPC measurement with two poly (S/divinylbenzene) gel columns (Phenogel 5 x $10^2$ and 3 x $10^5$ Å (pores), 7.8 mm (id) x 30 cm (length), Phenomenex, USA) connected in series and using THF as a mobile solvent. The flow rate of THF was maintained at 1.0 mL/min with column temperature control at 40 °C using refractive index detector (RI 2414, Water, USA). The experiment $M_n$ ($M_{n,\,exp}$) of PMAA-I and PMAA-*b*-PS was obtained by comparing with the calibration curve calibrated with 5 standard PS samples with molecular weights ranging from 500 to 300,000 g/mol.

The theoretical and experimental degree of polymerization ($DP_{th}$ and $DP_{exp}$) and number-average molecular weight ($M_{n,th}$) of PMAA-I were calculated by the equation 3.2,3.3 and 3.4, respectively. For $M_{n,th}$ of PMAA-*b*-PS was calculated by the equation 3.5[48]

$$DP_{th} = \frac{[\text{Mole of MAA}]}{[\text{Mole of CHI}_3]} \qquad (3.2)$$

$$DP_{exp} = \frac{(M_{n,exp}\text{ of PMAA-I}) - \text{MW of I}}{\text{MW of MMA}} \qquad (3.3)$$

$$M_{\mathrm{n,th}} = \frac{[\text{Mole of MAA}] \times \text{MW of MAA} \times \text{conversion}}{[\text{Mole of CHI}_3]} \tag{3.4}$$

$$M_{\mathrm{n,th}} = M_{\mathrm{n,exp}}\ \text{of PMAA-I} + \frac{[\text{Mole of styrene}] \times \text{MW of styrene} \times \text{conversion}}{[\text{Mole of PMAA-I}]} \tag{3.5}$$

3.3.3.5 Chemical structure

The chemical structure and the identification of different components in PMAA-I and PMAA-*b*-PS after the methylation was characterized by $^1$H NMR and NMR DOSY technique, respectively. The all NMR experiments were verified at 25 °C and recording at 400 MHz on a Bruker Avance 400 spectrometer equipped with a n Bruker 5 mm BBFO probe and a gradient amplifier and using the bipolar longitudinal eddy current delay pulse sequence (BPLED) in DOSY-NMR. The TMS as internal standard and $CDCl_3$ as a solvent were used.

3.3.3.6 Particle size measurement

Weight-and number-average diameters ($d_w$ and $d_n$, respectively) were measured by DLS apparatus (Delsa nano C, Beckman) at the light scatting angle of 165° at room temperature. The emulsion samples approximately 1-2 drops were diluted with approximately 8 mL of distilled water before measurement. For the particle size to the obtain was converted the number of the particle ($N_p$) per liter by the equation 3.6 [82]

$$N_{\mathrm{p}} = \frac{6 \times \text{total mass polymer}}{\pi d_{\mathrm{n}}^{3} d_{\mathrm{p}}} \tag{3.6}$$

Where $d_n$ is the number average particle diameter (in cm) and $d_p$ is the density of polystyrene (1.045 g/cm$^3$).

3.3.3.7 Zeta potential measurement

The Zeta potential measurement of PMAA-*b*-PS particles emulsion were measured with Zeta seizer apparatus (Delsa nano C, Beckman) in DI water, at 25 °C.

### 3.3.3.6 Morphology

The morphology of PMAA-*b*-PS particles was observed with SEM, AFM and TEM. For SEM observation, dried PMAA-*b*-PS particles were placed on the stub before coated with gold. The image was finally taken with SEM using appropriate magnification. For the AFM images, the polymers emulsion were prepared by a drop onto silicon wafers and dried at room temperature in a desiccator before observed with AFM at using Multimode 8 AFM from Bruker in a Peak Force Quantitative Nano Mechanics mode. For TEM images, emulsion was diluted to approximately 50 ppm, and then a drop was placed on a carbon-coated copper grid and dried at room temperature in a desiccator before observed with TEM.

# CHAPTER 4
# RESULT AND DISCUSSIONS

In this work, we focused on the preparation of PMAA-*b*-PS block copolymer particles to obtain narrow MWD and good colloidal stability via emulsifier-free emulsion polymerization. The polymerization was divided into two steps. Firstly, PMAA-I was prepared by solution polymerization and used as a macro chain transfer agent in the emulsion step. Secondly, the PMAA-*b*-PS particles were then prepared by emulsion ITP. The influence of the continuous phase pH, the utilization of PMAA-I with and without the purification, and the post addition of $CHI_3$ after polymerization were investigated.

## 4.1 Investigation of PMAA-I preparation by solution ITP and RTCP

In this step, two kinds of the polymerization as solution ITP and RTCP were used and compared for the preparation of PMAA-I macro chain transfer agent. As mentioned in the induction part, solution RTCP differed from solution ITP by the addition of a catalyst as a $Gel_4$. The possible mechanisms of both solution ITP and RTCP were shown in Figure 4.1 and 4.2, respectively. A V-70 as an initiator was firstly decomposed giving primary radicals (V-70•; Figure 4.1 (a)). The polymerization then proceeded with the existence of monomer (MAA) giving the active species as V-70-PMAA• (Figure 4.1 (b)). Meanwhile, the given active species were then end-capped by iodine radical derived from the existed $CHI_3$ giving dormant species (Figure 4.1 (c)) and the new radicals as $CHI_2$ radical ($CHI_2$•; Figure 4.1 (d)). The new active species (Figure 4.1 (e)) were then obtained by the addition of MAA monomer onto $CHI_2$ radical which is similar to that derived from the primary radical. Thereafter, iodine radicals then transfer between dormant (Figure4.1 (c)) and active (Figure4.1 (b) or (e)) chains where the obtained polymer represented control and livingness nature based on the exchange frequency of iodine radicals.

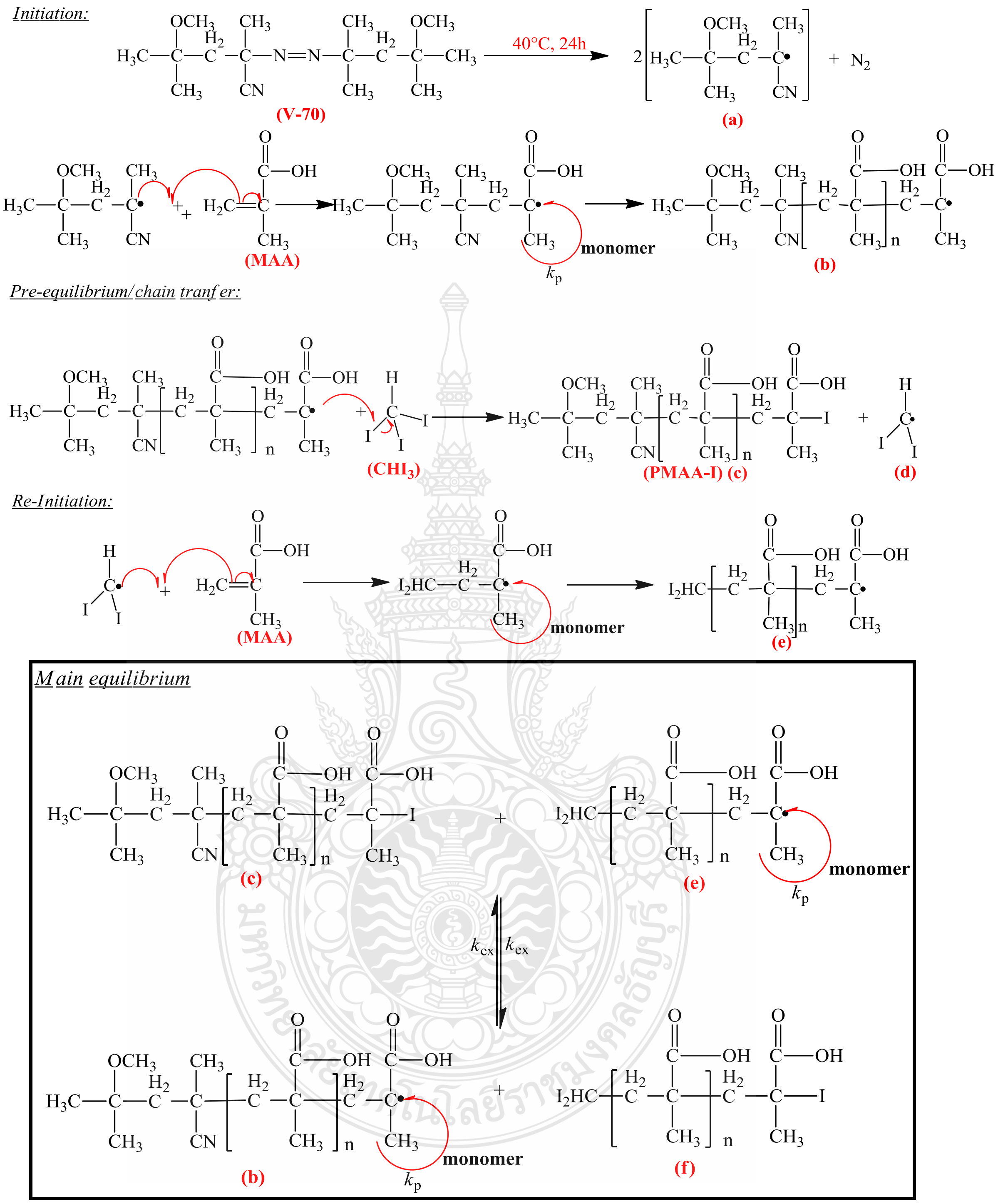


**Figure 4.1** Schematic illustration of the preparation of PMAA-I by solution ITP: V-70radical (a), V-70-PMAA radical as active species (b), V-70 PMAA-I as dormant species (c), $CHI_2$ radical (d), $CHI_2$-PMAA radical as active species (e) and $CHI_2$-PMAA-I as dormant species (f)

In the case of solution RTCP, it is similar to solution ITP except for the addition of $GeI_4$ into ITP system. The active chain V-70-PMAA• (Figure 4.1 (b)) or $CHI_2$-PMAA• (Figure 4.1 (e)) were end-capped by iodine radical dissociated from $GeI_4$ which deactivated to be dormant chains as V-70-PMAA-I (Figure 4.2 (c) or $CHI_2$-PMAA-I (Figure 4.2 (f)) including the activator $GeI_3$•. On the other hand, the activation reaction proceeded when the end chain iodine (I) of the dormant chains transferred to $GeI_3$• to be $GeI_4$ and to give the active chains again as shown in Figure 4.2. Because of faster transfer between active chains and catalyst radical ($GeI_3$•) of iodine radical for RTCP than that between two active chains of ITP, the cycle of activation/deactivation frequency was quite higher than the cycle of exchange frequency of ITP. Therefore, the better control and livingness nature of the obtained polymer was expected in the case of RTCP.

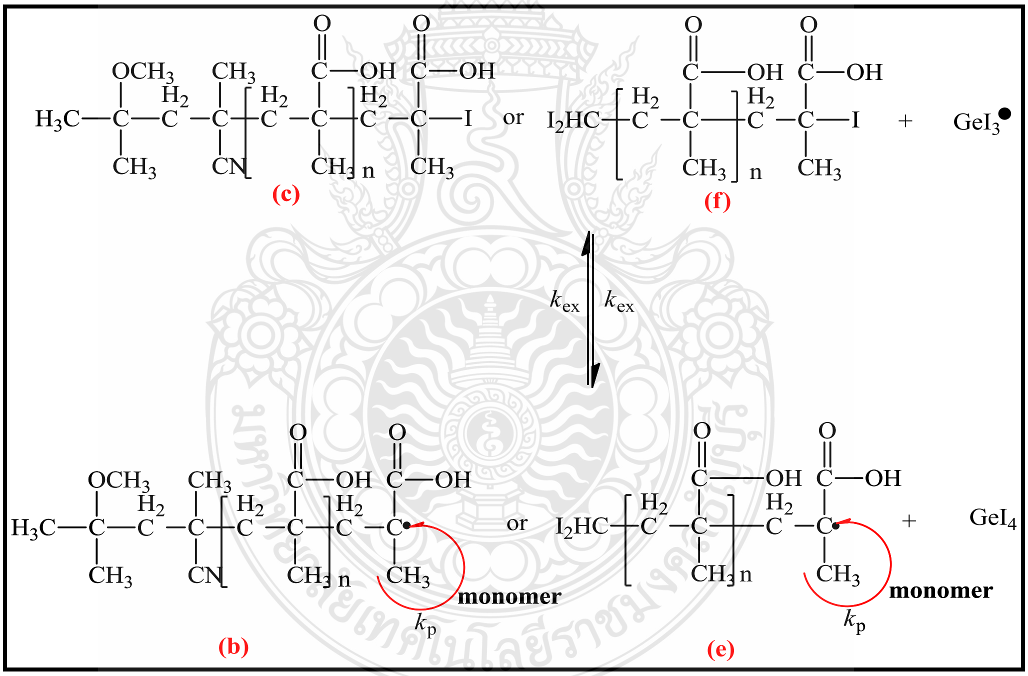


**Figure 4.2** Schematic illustration of the preparation of PMAA-I by solution RTCP; V-70-PMAA radical as active species (b), V-70-PMAA-I as dormant (c), $CHI_2$-PMAA radical as active species (e) and $CHI_2$-PMAA-I as dormant species (f)

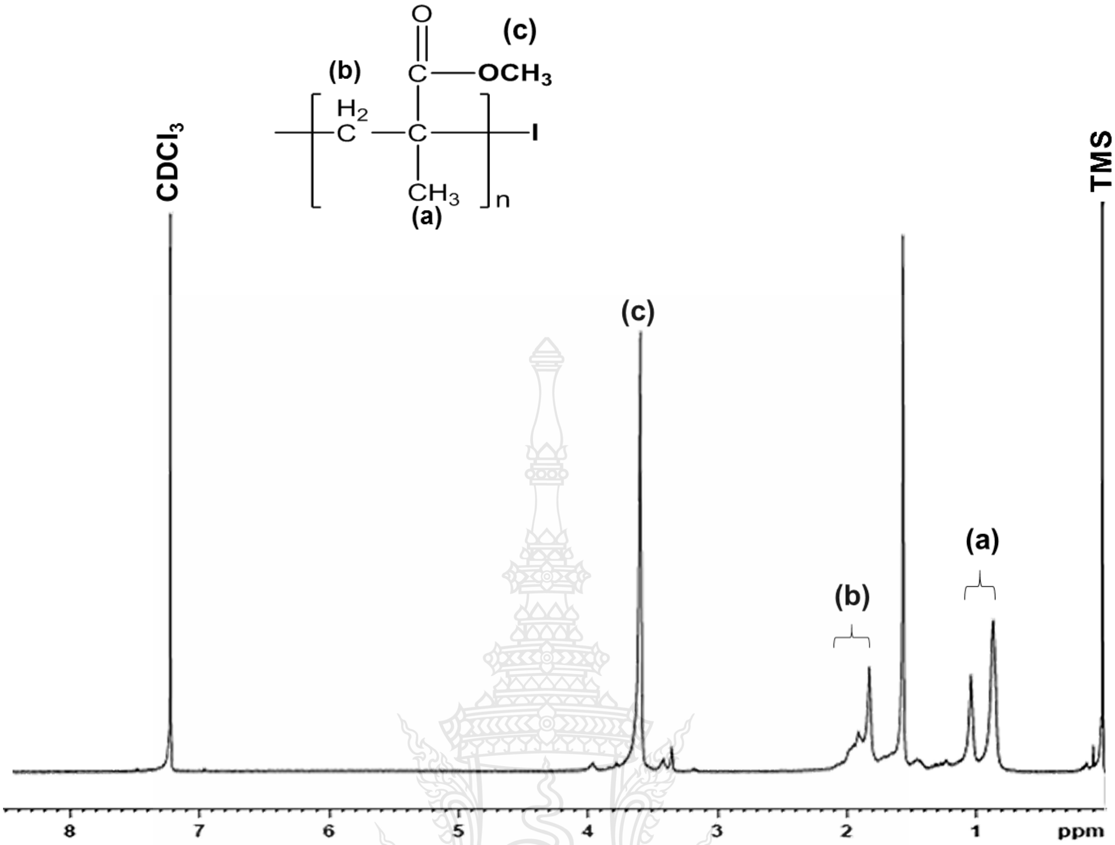


**Figure 4.3** $^{1}$H NMR spectra of PMMA-I (after methylation with TMSD) obtained by solution ITP

For both solution ITP and RTCP, the polymerizations smoothly proceeded and the monomer conversion attained at 100% for 24 h. Before GPC measurement, the hydrophilic PMAA-I chain was modified to form a more hydrophobic PMMA-I chain in order to dissolve in a THF GPC solution. In fact, the carboxyl group of MAA unit was methylated to be a methyl group. The $^{1}$H NMR spectra (Figure 4.3) of PMMA-I was used to confirm the methylation reaction. In the characteristic peaks of chemical shift at 3.6 ppm corresponds to the methoxy protons (-$OCH_3$) whereas at the region 1.7-2.1 ppm and 0.8-1.2 ppm represented methylene and methyl protons of -$CH_2$ and -$CH_3$, respectively. The result confirmed that PMAA-I was successfully synthesized and completely methylated, although the signal of I peak was not whatever observed.

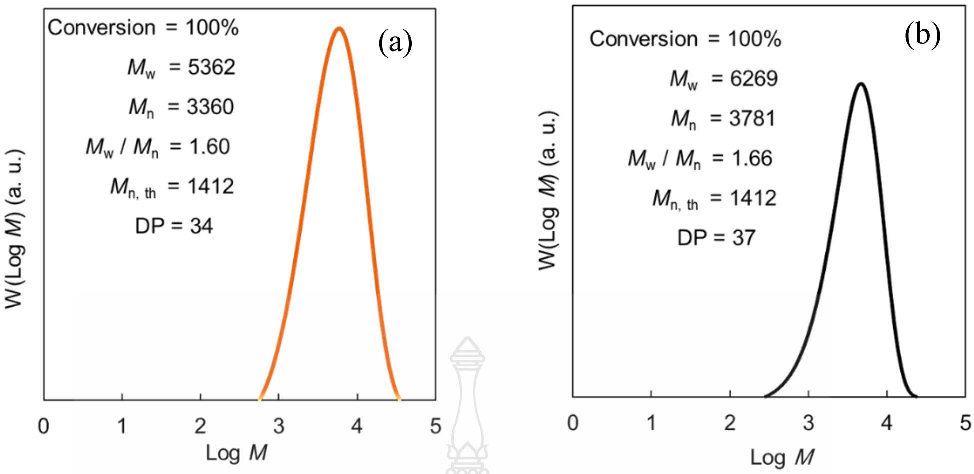


**Figure 4.4** MWD of PMMA-I (after methylation with TMSD) synthesized by solution ITP (a) and RTCP (b)

The MWD, $M_n$ and $M_w/M_n$ of the obtained PMAA-I prepared by both solution ITP and RTCP were shown in Figure 4.4 (a) and (b), respectively. In the case of solution ITP, the $M_n$ of the obtained PMAA-I was approximately 3,400 g/mol (corresponding to ca. 34 units of MAA (PMAA$_{34}$-I)) and higher than the $M_{n,\ th}$. In addition, the obtained $M_w/M_n$ (1.60) was rather high. However, those values were not improved with solution RTCP where $M_n$ and $M_w/M_n$ were ca. 3800 g/mol (corresponding to ca. 37 units of MAA (PMAA$_{37}$-I)) and 1.66, respectively. In fact, it is also difficult to obtain the difference performance between ITP and RTCP with the low $M_n$ of the target molecular weight. At high target $M_n$, RTCP may represent higher control and livingness nature than ITP. Therefore, in this step, solution ITP is enough to produce the PMAA-I macro chain transfer agent for using in the further emulsion ITP.

## 4.2 Preparation of PMAA-*b*-PS particles by emulsion ITP using PMAA-I as a macro chain transfer agent

The polymerization of styrene (S) was carried out at 60 °C, using PMAA-I as a macro chain transfer agent, and V-501 as an initiator of emulsion ITP. In this polymerization, the V-501 was firstly decomposed to give primary radicals (V-501•; Fig.4.5 (a)) before added with styrene to form V501-PS• (Fig.4.5 (b)) as active species in continues (aqueous) phase. In the meantime, the active species were then end-capped by

I radical derived from the exiting PMAA-I giving dormant species (Fig.4.5 (c)), resulting in the new radicals as PMAA• (Fig.4.5 (d)). The PMAA• can be reacted with styrene monomer which is similar to that derived from the primary radical, resulting in the new active species. Thereafter, iodine radicals then transfer between both dormant (Fig.4.5 (c)) and active (Fig.4.5 (b) or (d)) chains where the obtained polymer represented control and livingness nature base on the exchange frequency of iodine radicals. For this step, the influence of the pH (acidic and alkaline condition) and the utilization of PMAA-I solution with and without the purification were studied.

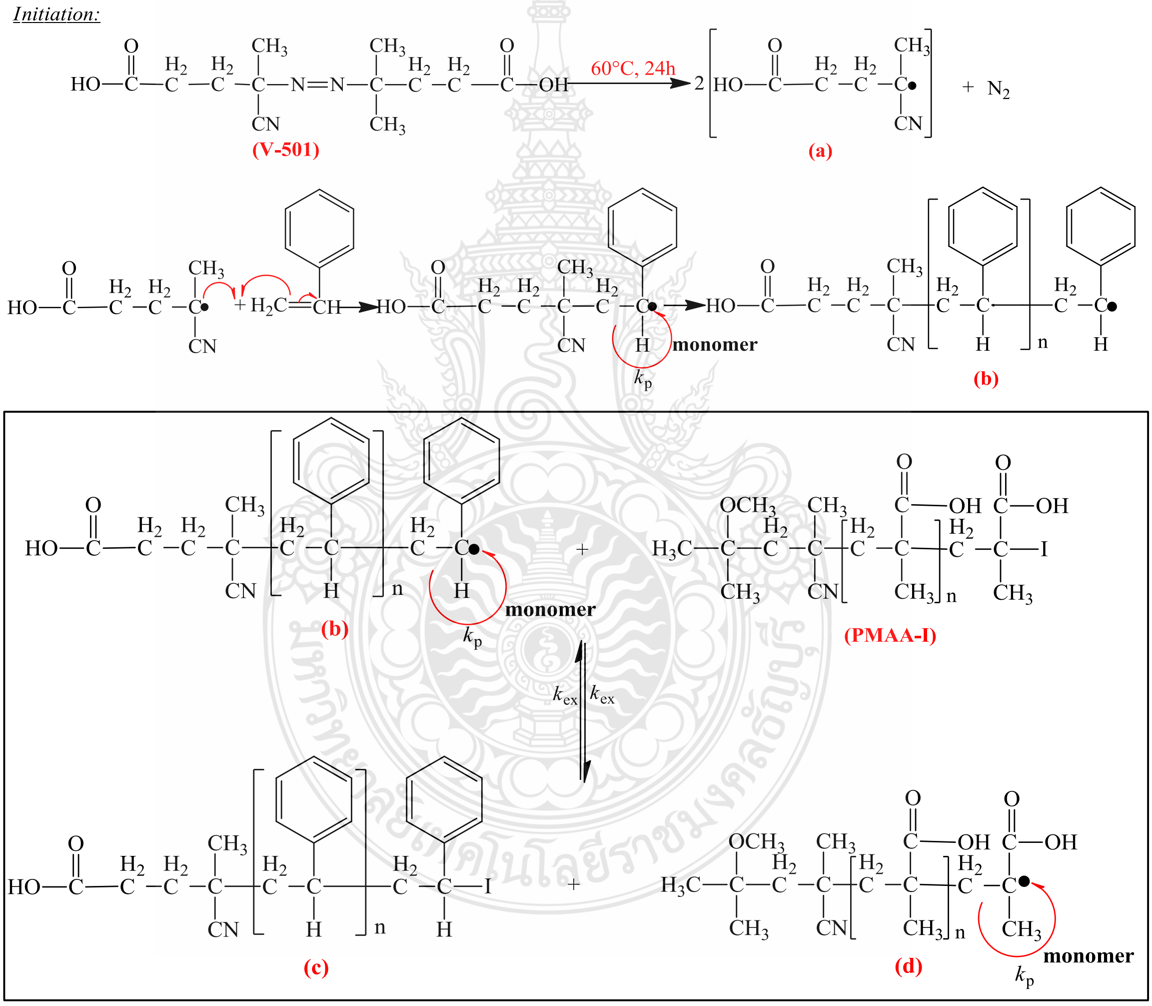


**Figure 4.5** Schematic illustration of the preparation of PMAA-*b*-PS by emulsion ITP: V-501 radical (a), V-501-PS radical as active species (b), V-501-PS-I as dormant species (c) V-70-PMAA-I as radical as active species (d)

### 4.2.1. Effect of continuous aqueous pH at acidic and alkaline condition

For this step, the preparation of PMAA-*b*-PS particles in emulsion ITP was polymerized at acidic (pH~4) and alkaline (pH~9, adjust pH by KOH) conditions. Figure 4.6 shows conversion versus time plots of emulsion ITP of styrene using PMAA-I as a macro chain transfer agent and V-501 as an initiator at both conditions. At the pH~4, the polymerization slowly proceeded and reached 45% conversion for 24 h, which was much slower than that of pH~9 (100% conversion for 24 h).

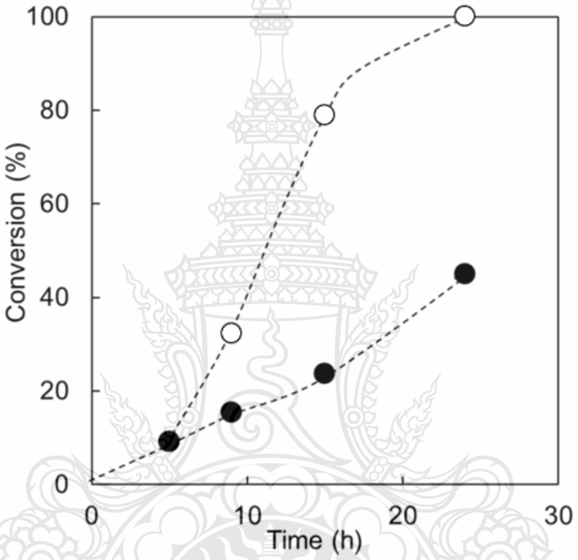


**Figure 4.6** Conversion versus time plots of PMAA-*b*-PS prepared by emulsion ITP at 60°C at pH~4 (closed circles) and pH~9 (open circles) using styrene/PMAA-I/V-501 (molar ratio) = 400/1/1

**Table 4.1** Weight - and number - average diameter ($d_{\mathrm{w}}$ and $d_{\mathrm{n}}$, respectively)), size distribution ($d_{\mathrm{w}}/d_{\mathrm{n}}$), numbers of particles ($N_{\mathrm{p}}$) and zeta potential of PMAA-*b*-PS particles obtained by emulsion ITP using PMAA-I (without purification) macro chain transfer and V-501 initiator under uncontrol pH (pH~4) and control pH (pH~9) conditions at each conversion

| **Conditions** | **Conversion (%)** | **$d_{\mathrm{w}}$ (nm)** | **$d_{\mathrm{n}}$ (nm)** | **$d_{\mathrm{w}}/d_{\mathrm{n}}$** | **$N_p$x$10^{13}$ ($L^{-1}$)** | **Zeta potential (mV)** |
|---|---|---|---|---|---|---|
| acidic, (pH 4) | 9 | 720 | 714 | 1.01 | 4.38 | - |
| | 15 | 1,234 | 1,182 | 1.04 | 1.70 | - |
| | 24 | 2,203 | 1,804 | 1.35 | 0.73 | - |
| | | 180 | 98 | 1.85 | - | |
| | 45 | 4425 | 4,342 | 1.02 | 0.09 | -15 |
| alkaline, (pH 9) | 9 | 149 | 119 | 1.25 | 939 | - |
| | 32 | 183 | 137 | 1.34 | 2,223 | - |
| | 79 | 190 | 148 | 1.28 | 4,400 | - |
| | 100 | 250 | 223 | 1.12 | 1,635 | -42 |

Table 4.1 presented the PMAA-*b*-PS particle size obtained by emulsion ITP at the acidic (pH~4) and alkaline (pH~9) conditions. For both cases, the particle size increased with the conversion. At pH~4, the particle size distribution (number distribution) had monomodal size distributions (Figure 4.7) with mainly micrometer-sized particles except at 24% conversion where the bimodal size distributions were observed. In the other hand, submicrometer-sized particles with monomodal size distributions for all conversion were obtained at pH (pH~9) (Figure 4.8). From the result, it clearly observes that the particle size of at pH (pH~4) was larger than that of at pH (pH~9). This phenomenon will be discussed a follows.

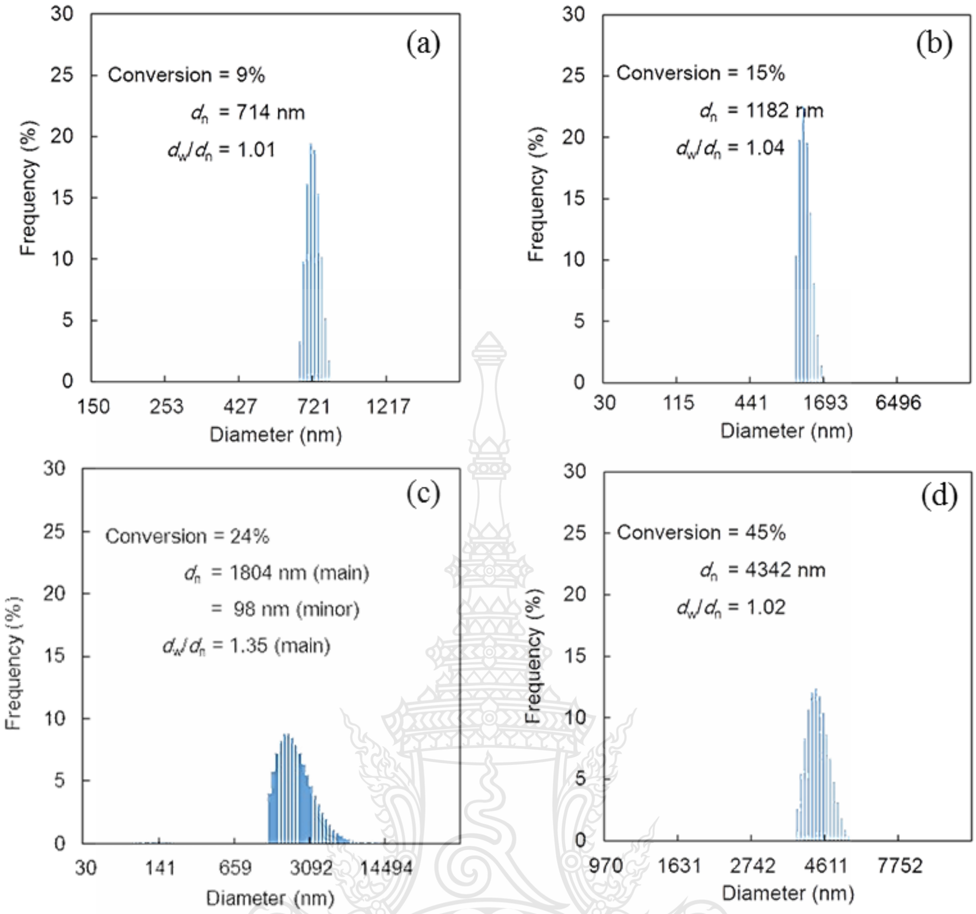


**Figure 4.7** Size distributions (number distribution; measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP using PMAA-I macro chain transfer agent V-501 initiator under uncontrol pH (pH~4) at different conversions (%): 9 (a), 15 (b), 24 (c), and 45 (d)

Both the particle nucleation of homogeneous nucleation of PS chains without PMAA-block (the larger size) and self-assembly nucleation of PMAA-*b*-PS (smaller size; ~100-200 nm) seemed occurring throughout the polymerization at pH 4 according to previous works [48]. In an early stage of the polymerization, both particle formations were not significantly different. However, particle coagulation would be the main reason to obtain the higher number of the larger particle than that of the smaller one although a bimodal of size distributions was only observed at 24 % conversion. After 24 % conversion, the smaller size particles apparently disappeared because of adsorption onto the bigger size particles. The size of the remained particles (micrometer-size) increased with the conversion based on not only the polymerization but also the coalescence among the unstable smaller particles of block copolymer self-assembly, unstable homogenous nucleated particles, and unstable larger particles. Moreover, the *N*p was quite low at an early stage (conversion of 9%) of the polymerization (Table4.1) and gradually decreased with increasing of conversion. These indicate that the coagulation of particles began from the initial stage and continued throughout the polymerization, resulting in the polymer particle with low colloidal stability. The zeta potential (-15 mV) of the particle at the final conversion was also confirmed that the obtained particle in this condition was low colloidal stability. This phenomenon was clearly observed by SEM photograph (Figure 4.10 (a)) where cluster particle was mainly obtained. This is because $pK_a$ of PMAA in an aqueous solution is 5.55-5.65 [83, 84]. At the pH~4 the carboxyl groups of PMAA-I hardly ionize. Therefore, under this condition, PMAA chains do not operate effectively to stabilize forming particles as the hairy layer at the particle surfaces. Moreover, a part of the unionized PMAA-I may adsorb at the interface of styrene droplets and cannot act as the macro chain transfer agent. It then reduced the efficiency of the particle formation via self-assembly of the low molecular amphiphilic block copolymer or PMAA-*b*-PS-I in the aqueous medium in the early stage of the polymerization. In addition, the adsorbed PMAA-I desorbs from the monomer droplet surface due to a decrease of surface area of the droplets, which operate as monomer reservoir. The formation of new particles with the self-assembly of PMAA-*b*-PS-I was thus obtained throughout the polymerization until monomer droplets disappear in the system. Although, most of the smaller sizes were not detected with DLS in all conversions except at 24 % conversion. In fact, at 24% conversion, the number of formed particles nucleated with both mechanisms may not significantly different where the MWD curve having a shoulder at the higher molecular weight (homogeneous nucleation) was clearly observed as shown in Figure 4.8 (a). Thereafter, $M_w/M_n$ value attained 3 at 45% conversion although $M_n$ values were apparently closed to $M_{n,th}$ value and linearly increased with the conversion (shown in Figure 4.8 (b)).

**Table 4.2** The $M_{n,}$ and $M_w/M_n$ of PMAA-*b*-PS (after methylation) obtained by emulsion ITP using PMAA-I (without purification) macro chain transfer and V-501 initiator under uncontrol pH (pH~4) and control pH (pH~9) condition at each conversion.

| Conditions | Time (h) | Conversion (%) | $M_{n,\ th}$ | $M_{n,\ exp}$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| Un-control pH, (pH 4) | 5 | 9 | 7,670 | 8,900 | 1.40 |
| | 9 | 15 | 10,200 | 12,900 | 1.96 |
| | 13 | 24 | 13,700 | 13,800 | 2.19 |
| | 24 | 45 | 22,500 | 27,600 | 3.09 |
| Control pH, (pH 9) | 5 | 9 | 7,400 | 8,100 | 1.49 |
| | 9 | 32 | 17,000 | 18,500 | 2.10 |
| | 15 | 79 | 36,500 | 36,700 | 2.19 |
| | 24 | 100 | 45,400 | 46,600 | 2.10 |

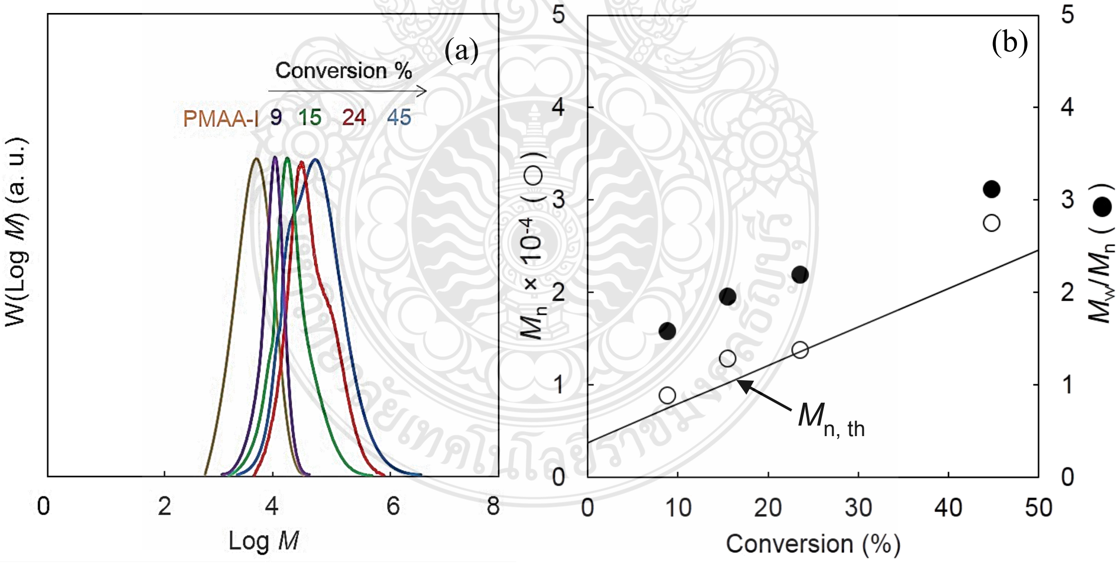


**Figure 4.8** MWDs (a), $M_n$ (open circles) and $M_w/M_n$ (closed circles) (b) at different conversions of PMMA-*b*-PS (after methylation TMSD) prepared by emulsion ITP using PMAAI macro chain transfer agent and V-501 initiator at 60 °C under acidic condition (pH~4) using styrene/PMAA -I/V-501 (molar ratio) = 400/1/1

On the other hand, when the emulsion ITP was carried out at pH~9, at which all of the carboxyl groups of PMAA-I ionize, $d_n$ values of PS particles were 119 nm, 137 nm, 148 nm and 223 nm at 9%, 32% and 79%, 100% conversions, respectively (Table 4.1). Moreover, monomodal particle size distribution was maintained throughout the polymerization (Figure 4.9 (a-d)), which accorded with TEM photograph (Figure 4.10 (b)) at final conversion. The particles were spherical in shape with a sub-micrometer size. In addition, particle agglomeration did not occur. It is seen that the polymer particle was good colloidal stability. This result indicated that a larger number of the ionized carboxyl group of PMAA-I chain are given at pH~9, causing the formed particles with much more stable than at pH~4.

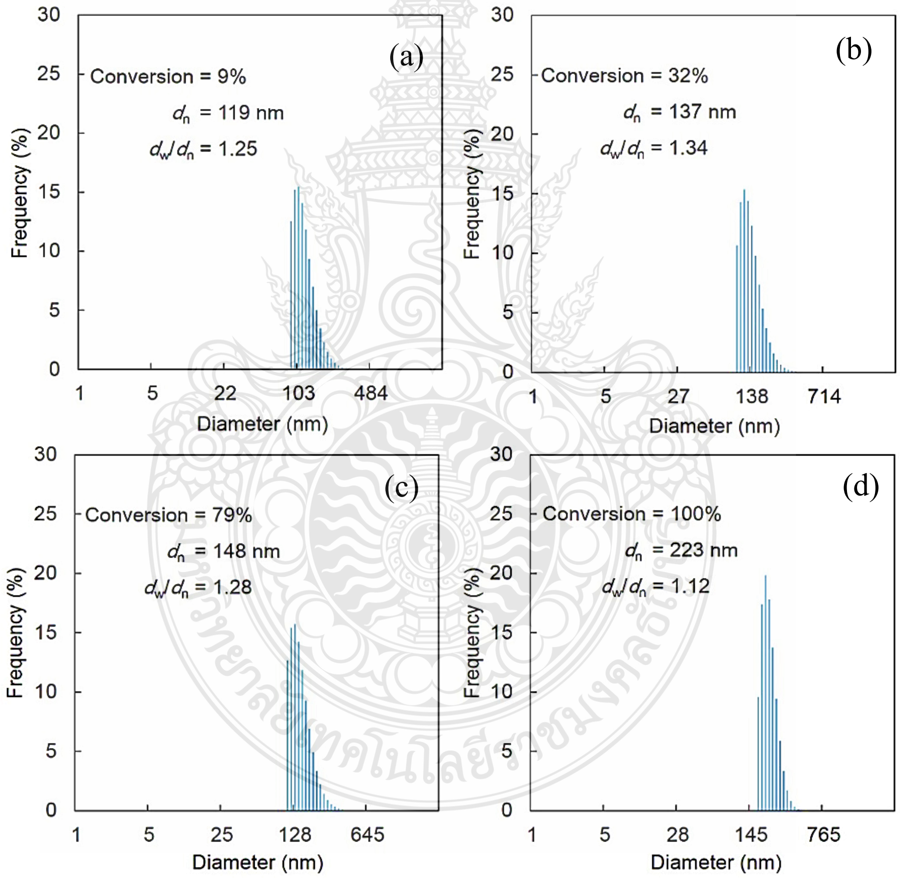


**Figure 4.9** Size distributions (number distribution; measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP using PMAA-I macro chain transfer agent and V-501 initiator at 60 °C under control pH (pH~9) at different conversions (%): 9 (a), 32 (b), 79( c), and 100 (d)

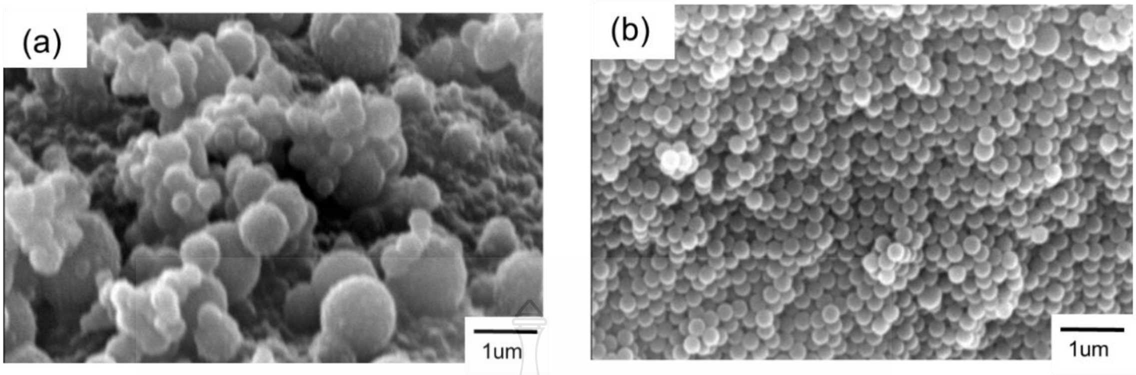


**Figure 4.10** SEM photographs of PMAA-*b*-PS particles prepared by emulsion ITP pH 4 (a) and pH 9 (b)

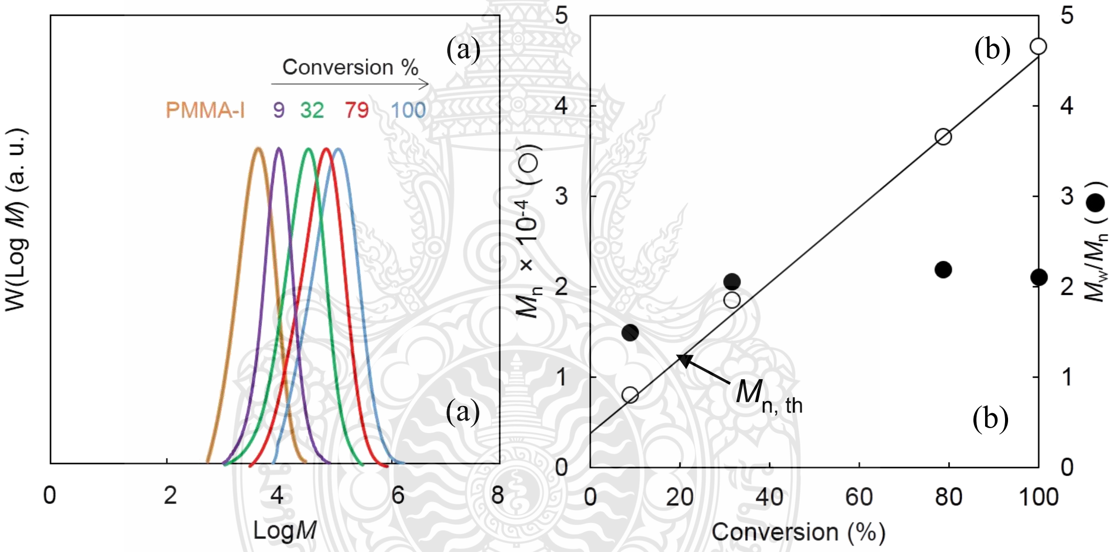


**Figure 4.11** MWDs (a), $M_n$ (open circles) and $M_w/M_n$ (closed circles) (b) at different conversions of PMMA-*b*-PS (after methylation TMSD) prepared by emulsion ITP using PMAA-I macro chain transfer agent and V-501 initiator at 60 °C undecontrol pH (pH~9) using styrene/PMAA -I/V-501 (molar ratio) = 400/1/1

In addition, Figure 4.11 shows MWDs, $M_n$ and $M_w/M_n$ at different conversions of the emulsion ITP at pH~9. The MWD, in which any shoulder was not observed at each conversion, shifted to the higher molecular weight maintaining a relatively narrow distribution with increasing conversion. The $M_n$ value increased linearly with conversion and well agreed with the $M_{n,th}$ at each conversion (Figure 4.11(b)). The $M_w/M_n$ values were relatively low (~2.1) throughout the polymerization. Although, the molecular weight of PMMA-*b*-PS (after methylation) measured by GPC using PS standard may not linearly correlate to their absolute molecular weight. However, because the PMMA-*b*-PS prepared in this study has a short PMMA block (degree of polymerization was 34) in comparison with PS block, the obtained $M_n$ would not be significantly different from the absolute one. By the comparison with PMMA-I (after methylation), MWD of PMAA-*b*-PS shifted to higher molecular weight with keeping a narrow MWD even at 9% conversion, where the weights of original PMAA-I and PS in the system were nearly the same. There was no shoulder at the lower molecular weight side in the MWD at 9% conversion. The result indicates that most of PMAA-I acted as the macro chain transfer agent in the early stage of the emulsion ITP and added styrene monomers, resulting in PMAA-*b*-PS. That is, the emulsion ITP using PMAA$_{37}$-I macro chain transfer agent proceeded with some living features at the alkaline condition. In addition figure 4.12 (a) and (b) presented $^1$H NMR spectra of PMMA-I and PMMA-*b*-PS (after methylation) prepared by the solution ITP and emulsion ITP, respectively. The characteristic peaks of PMMA in Figure 4.12 (a) shown that the peak at 3.6 ppm, around 1.7 and 2.1, and around 0.8-1.2 correspond to three protons of methoxy proton (-OCH$_3$), two protons (-CH$_2$) and three protons (-CH$_3$) of methyl proton, respectively. For PMAA-*b*-PS (Figure 4.12 (b)), all characteristic peaks of MMA were observed. Moreover, the additional peaks at 6.5–7.2 ppm and at 1.5-2 ppm corresponded to the characteristic peak for five protons of the phenyl ring and methylene and methyl groups of PS, respectively [85]. Based on the $^1$H NMR spectra, it was confirmed that PMMA-*b*-PS was successfully synthesized by emulsion ITP using PMAA-I as macro chain transfer agent via self-assembly nucleation.

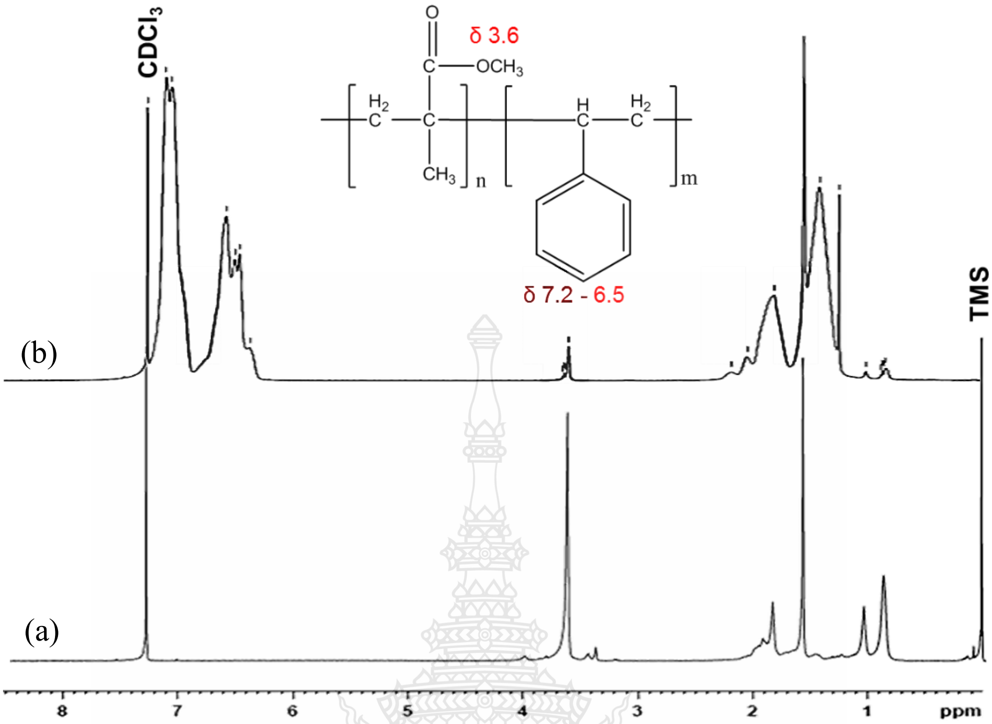


**Figure 4.12** $^1$H NMR spectra after methylation with TMSD of PMMA-I prepared by solution (a) and PMAA-*b*-PS (b) prepared by emulsion ITP using PMAA-I at 60 °C under pH~9 (with KOH) at final conversion

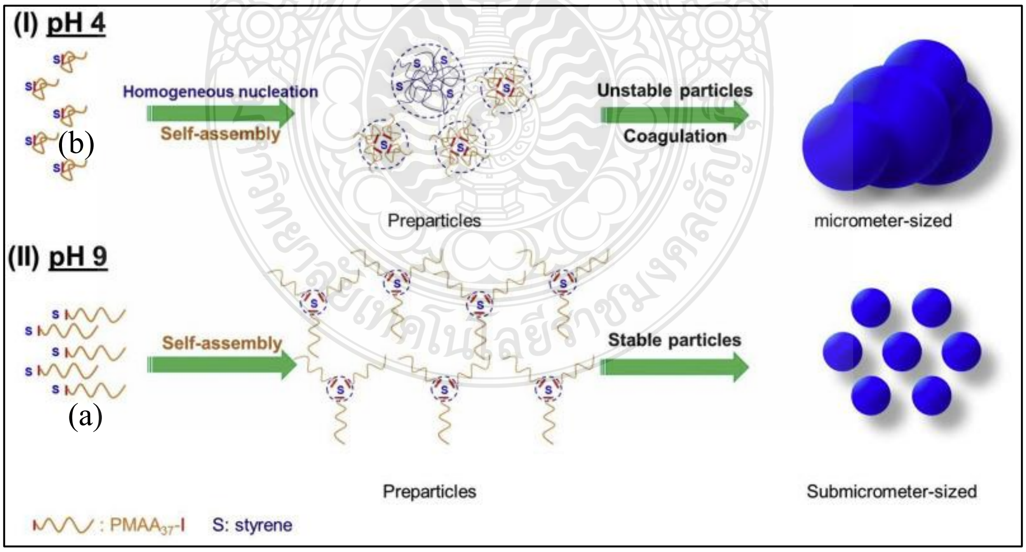


**Figure 4.13** Schematic of emulsion ITP with self-assembly nucleation at acidic or alkaline pH

From this study, it is concluded that the using PMMA-I as a macro chain transfer agent and V-501 as an initiator at 60 °C was successfully carried out with self-assembly nucleation at the alkaline condition (pH~9). The polymerization reached to high conversion maintaining good control/livingness features, with good colloidal stability without coagulation occurred. The mechanism proposed for emulsion ITP with self-assembly nucleation at both pH is illustrated in Figure 4.13. In addition, at alkaline condition (pH~9) was selected as optimum polymerization condition for further study.

#### 4.2.2 Using PMAA-I with and without purification as a macro chain transfer agent for the preparation of PMAA-*b*-PS particles by emulsion ITP

In the previous part, PMAA-*b*-PS particle using PMAA-I as macro chain transfer agent was successfully prepared at the alkaline condition (pH~9). The MWD shifted to the higher with increasing the conversion with the living nature. However, the $M_w/M_n$ value of the obtained PMAA-*b*-PS was still quite high (approximately 2.1). This seemed that ITP may lose activity during emulsion polymerization. Therefore, a further experiment was used to clarify this phenomenon. In solution ITP of PMAA-I, all iodine radicals initiated from $CHI_3$ were expected to participate in the polymerization as end-capping PMAA chains, (PMAA-I). In fact, after the addition PMAA-I solution (from solution ITP) into an alkaline aqueous solution, a large amount of $CHI_3$ precipitated out (Figure 4.14). After several hours, $CHI_3$ might move into the formed PMAA-*b*-PS particle as the disappearance of a precipitated compound in an aqueous medium. This may the reason why the living nature of PMAA-*b*-PS still obtained. In the early stage of emulsion ITP, some of iodine radical participate the polymerization as end-capping on the PMAA chains. After pre-particles were formed based on self-assembly of PMAA-*b*-PS containing iodine radical, the precipitated $CHI_3$ might smoothly diffuse into the particles where iodine radical can be generated to act as chain transfer agent therein. The increase of total surface area of the hydrophobic part as increasing the number of particles increased the diffusion rate of $CHI_3$ into the polymer particles. However, a long period of precipitation would reduce the activity of $CHI_3$ which resulted in quite high $M_w/M_n$ of PMAA-*b*-PS.

**Figure 4.14** Emulsion ITP photo after the addition of PMMA-I solution

**Table 4.3** %Yield of PMAA-I obtained by the precipitation of solution ITP

| No. | Solution ITP (g) | PMAA-I (g) | | Yield PMAA-I (%) |
|---|---|---|---|---|
| | | Theoretical | Experimental | |
| 1 | 3.20 | 0.42 | 0.42 | 100 |
| 2 | 3.40 | 0.44 | 0.43 | 98 |
| 3 | 3.40 | 0.44 | 0.42 | 95 |
| **Average** | | | | **98** |

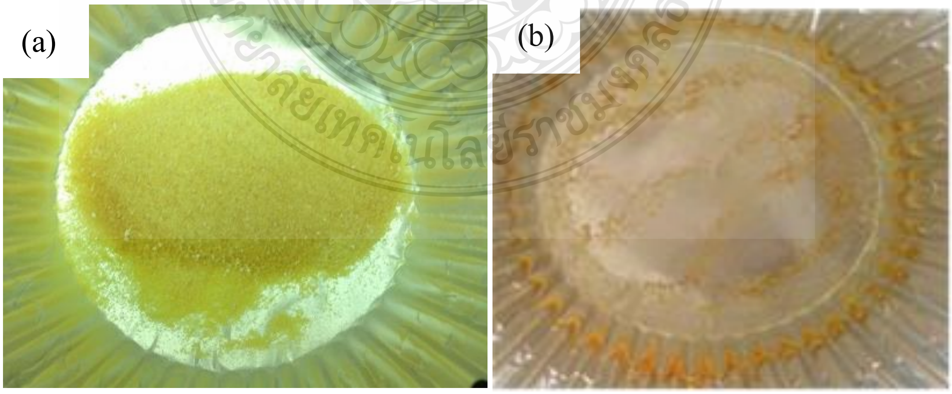


**Figure 4.15** PMAA-I (a) and unreacted $CHI_3$ (b) after purification of solution ITP

To clarify this issue, the content of the reacted (in term of PMAA-I) and unreacted $CHI_3$ from solution ITP was first measured. PMAA-I could be separated out from the solution by the precipitation in diethyl ether where the unreacted $CHI_3$ was still soluble in solution ITP. The yellow powder of PMAA-I (Fig. 4.15 (a)) was obtained after dried the precipitated compound whereas after dioxane-diethyl ether mixture solvent was evaporated, the dried orange of unreacted $CHI_3$ (Fig. 4.15 (b)) was observed. In addition, the detail of the PMAA-I and the unreacted $CHI_3$ contents in the solution ITP were shown in Table 4.3 and 4.4, respectively. Based on the high monomer conversion, the experimental PMAA-I obtained after purification closed to the initial amount of monomer (98%). However, only about 36% of the initial $CHI_3$ was end-capped on the PMAA-I chains. This is the reason why a large amount (64%) of the precipitated $CHI_3$ in an alkaline solution of emulsion ITP was observed. Based on the low content of reacted $CHI_3$ in emulsion ITP, the polymerization of PMAA-*b*-PS was the low performance of the control (quite broad MWD) as shown in the previous part. Although, most of the unreacted $CHI_3$ diffused into the polymerizing particle after the particle formation. The following experiment was carried out to evaluate the performance of the unreacted $CHI_3$ in emulsion ITP. The emulsion ITP of PMAA-*b*-PS using purified PMAA-I was studied compared with using unpurified PMAA-I.

**Table 4.4** % Remained $CHI_3$ in solution ITP after separation of PMAA-I

| **No.** | **Solution ITP (g)** | **$CHI_3$ (mmol)** | | **Remained of $CHI_3$ (%)** |
|---|---|---|---|---|
| | | Initial $CHI_3$ | Remained $CHI_3$ | |
| 1 | 3.2 | 0.32 | 0.21 | 65 |
| 2 | 3.4 | 0.34 | 0.22 | 63 |
| 3 | 3.4 | 0.34 | 0.21 | 64 |
| **Average** | | | | **64** |

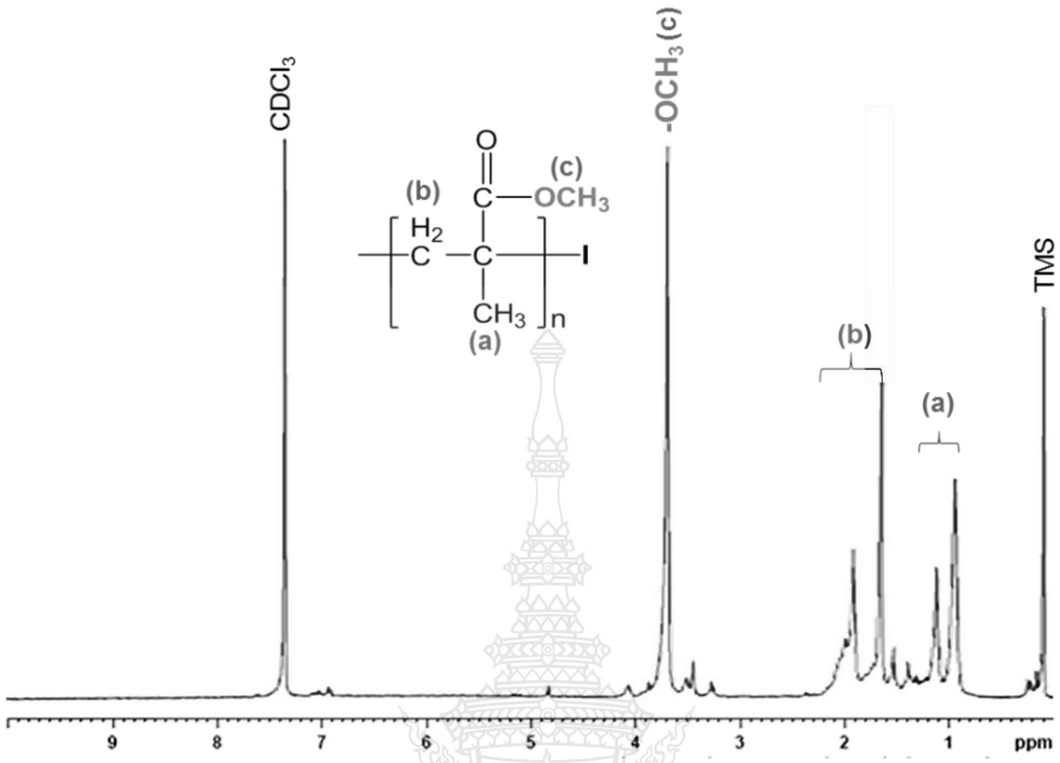


**Figure 4.16** $^1$H NMR spectra of the purified PMMA-I (after methylation with TMSD) obtained from solution ITP after removal the unreacted $CHI_3$

Before emulsion ITP, the obtained purified PMAA-I was characterized by $^1$H NMR as shown in Fig. 4.16 in which all important characteristic peaks were the same as those of the unpurified PMAA-I as observed in Fig. 4.4. It was confirmed that the purified PMMA-I was a similar structure to the unpurified PMAA-I. Thereafter, the purified PMAA-I was used as a macro chain transfer agent in emulsion ITP where the optimal condition of the previous part was used in this experiment.

Figure 4.17 showed conversion versus time plots of emulsion ITP using both purified and unpurified PMAA-I. Both polymerizations smoothly proceeded with a similar polymerization rate and reached the high conversion (%) within 24 h. In addition, the experimental $M_n$ of PMAA-*b*-PS was much higher than the theoretical value in the case of purified PMAA-I (Table 4.5). This seemed that lower content of iodine radical participated in the polymerization than using unpurified PMAA-I. The higher molecular weight of the obtained polymer was due to higher termination reaction.

However, the iodine radical represented high performance as a chain transfer agent because the $M_w/M_n$ (~2.2) of the obtained PMAA-*b*-PS was not different from that of the unpurified PMAA-I.

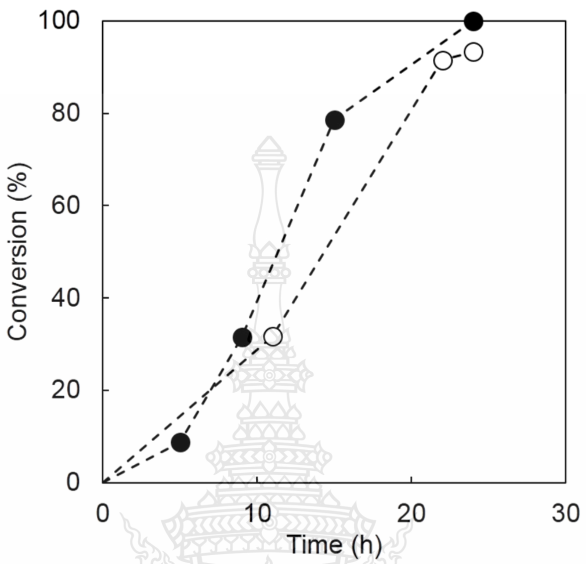


**Figure 4.17** Conversion versus time plots of PMAA-*b*-PS prepared by emulsion ITP using unpurified (open circles) and purified (closed circles) PMAA-I at 60°C using styrene/PMAA-I/V-501(molar ratio) = 400/1/1

**Table 4.5** The $M_{n,}$ and $M_w/M_n$ of PMAA-*b*-PS (after methylation) obtained by emulsion ITP using purified and unpurified PMMA-I macro chain transfer and V-501 initiator under control pH (pH~9) condition at each conversion

| PMAA-I | Conversion (%) | $M_{n, th}$ | $M_{n, exp}$ | $M_w/M_n$ |
|---|---|---|---|---|
| unpurified | 9 | 7,550 | 8,100 | 1.49 |
| | 32 | 17,400 | 18,500 | 2.10 |
| | 79 | 36,500 | 36,700 | 2.19 |
| | 100 | 45,400 | 46,600 | 2.10 |
| purified | 32 | 16,600 | 144,700 | 2.21 |
| | 92 | 41,500 | 209,600 | 2.23 |
| | 93 | 42,200 | 211,100 | 2.23 |

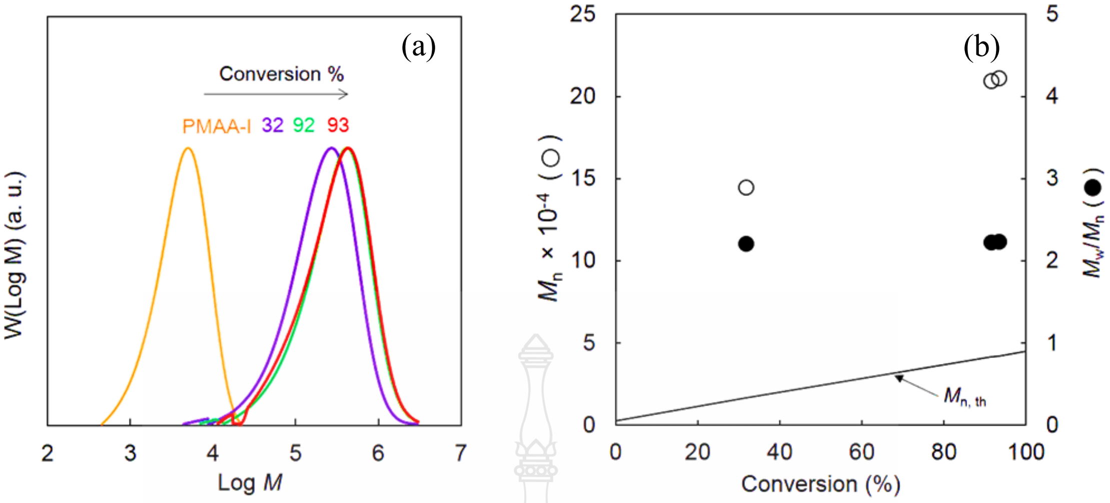


**Figure 4.18** MWDs (a) and $M_n$ (open circles) and $M_w/M_n$ (closed circles) (b) at different conversions of PMMA-*b*-PS (after methylation TMSD) prepared by emulsion ITP using purified PMAA-I macro chain transfer agent and V-501 initiator at 60 °C under pH~9 (with KOH) using styrene/PMAA-I/V-501(molar ratio) = 400/1/1

**Table 4.6** Particle size of PMAA-*b*-PS particles obtained by emulsion ITP of styrene using unpurified and purified PMAA-I macro chain transfer agent and V-501 initiator under at pH~9 (with KOH) condition at each conversion

| **Conditions** | **Time (h)** | **Conversion (%)** | **$d_n$ [a] (nm)** | **Size [b] (nm)** | **$N_p$x$10^{14}$ (L-1)** |
|---|---|---|---|---|---|
| Unpurified PMAA-I | 5 | 10 | 266 | 220-270 | 9.4 |
| | 11 | 27 | 502 | 460-520 | 3.6 |
| | 15 | 33 | 602 | 550-620 | 2.6 |
| | 22 | 45 | 607 | 500-620 | 3.5 |
| | 30 | 68 | 710 | 600-740 | 3.3 |
| Purified PMAA-I | 11 | 32 | 116 | 120-200 | 1214 |
| | 22 | 92 | 156 | 150-200 | 499 |
| | 24 | 93 | 178 | 120-200 | 336 |

[a] Measured by DLS

[b] Measured by AFM

In addition, the MWD (Fig. 4.18 (a)) and $M_n$ (Fig. 4.18 (b)) were shifted to higher molecular weight with increasing conversion. That is, the polymerization proceeded to maintain a livingness. PMMA-*b*-PS particle would mainly form based on self-assembly nucleation where only monomodal particle size distribution (Fig. 4.19) was observed throughout the polymerization. The particle size increased with the conversion without any coagulation. The narrow particle size distribution in the term of $d_w/d_n$ (~1.0) was obtained. MWD as $M_w/M_n$ (~2.2) seemed constant during the polymerization. This result indicated that the iodine radicals end-capped onto the purified PMAA-I chains were able to maintain the activity as similar as iodine radical of unpurified PMAA-I even though they were precipitated in ethyl ether. After particle formation in an aqueous medium via self-assembly of PMAA-*b*-PS, the PMAA segments were an anchor on the particle surface where the iodine radicals transferred among the polymerizing chains inside the particle. Moreover, using the purified PMAA-I seemed to present more performance for the stabilization of the formed particles where the smaller particle size (~3 times) measured by both DLS and AFM (Table 4.6) were obtained throughout the polymerization. The calculation $N_p$ (based on DLS measurement) was clearly seen that approximately 100 times higher than using unpurified PMAA-I. The particle morphology of the obtained PMAA-*b*-PS particles prepared by emulsion ITP using unpurified and purified PMAA-I was measured by AFM and TEM as shown in Figure 4.20. Both conditions, spherical particles were observed. Moreover, the particle size and size distribution prepared by purified PMAA-I were significantly smaller and narrower than those prepared by unpurified PMAA-I which accorded the DLS data explained in the previous time.

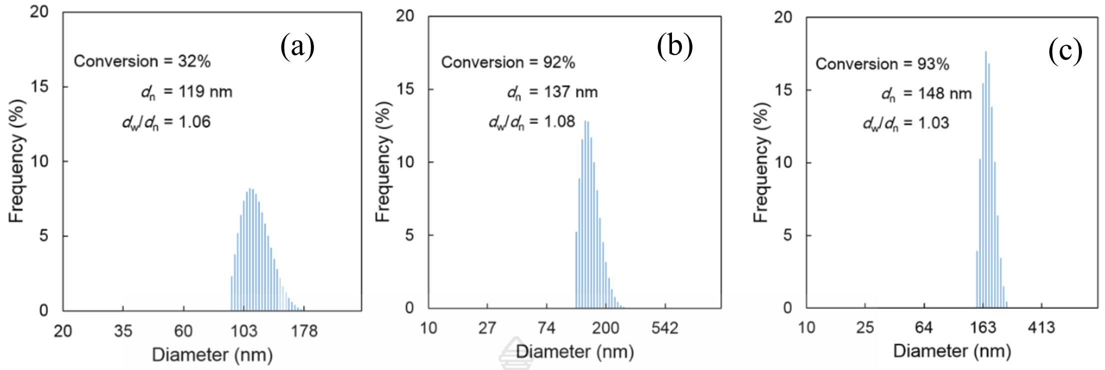


**Figure 4.19** Size distributions (number distribution; measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP using purified PMAA-I V-501 initiator at 60 °C under pH~9 (with KOH) at different conversions (%): 31 (a), 92 (b), 93 (c)

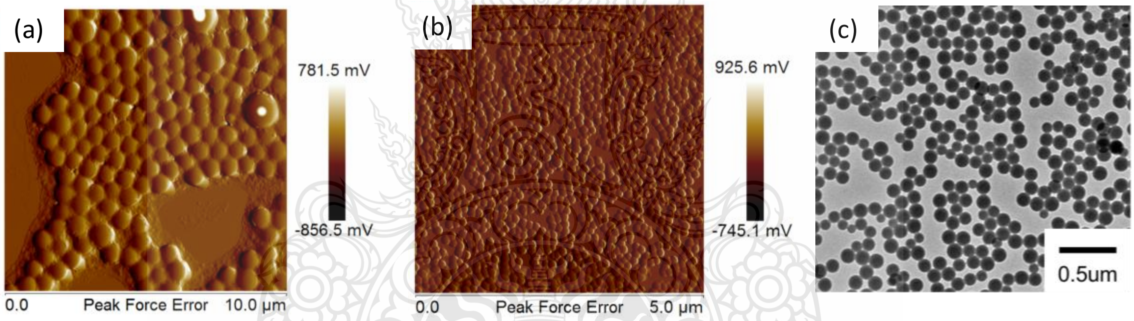


**Figure 4.20** AFM (a and b) and TEM (c) photographs of PMAA-*b*-PS particles prepared by emulsion ITP using unpurified (a) and purified (b and c) PMAA-I at 60°C under pH~9 (with KOH) at final conversion (%)

In addition, $^1$H NMR spectra of the obtained PMAA-*b*-PS particles prepared by emulsion ITP using purified PMAA-I as a macro chain transfer agent compared to original PMAA-I were showed in Fig.4.21. The characteristic peaks at 3.6 ppm corresponded to methoxy proton ($-OCH_3$) of PMAA was observed in both PMAA-I (Fig. 4.21 (a)) and PMAA-*b*-PS (Fig. 4.21(b)) spectra whereas the peaks for five protons of the phenyl ring in PS structure at 6.5–7.2 ppm were only observed in PMAA-*b*-PS (Fig. 4.21 (b)) spectrum. In addition, the intensity of the methoxy proton peak was lower in PMAA-*b*-PS than PMAA-I because the larger amount (the phenyl ring peak) of PS was extended in the polymer chains. This result was clearly observed with the two-dimension (DOSY) NMR spectra as shown in Fig.4.22. At the early stage of the polymerization, the characteristic peaks of both PMAA (methoxy proton) and PS (the phenyl ring) segments were in the same line (Fig. 4.22 (a)) whereas the main base peak of PS seems over than that of PMAA with the conversion. In addition, the intensity of PS peak was clearly larger than the PMAA peak, especially at the final conversion. This confirmed the assumption that the PS segment was not different from PMAA segment in the early stage of the polymerization. However, after the particle formation where the particle swelled with styrene monomer, only PS was polymerized in the inside of the particles.

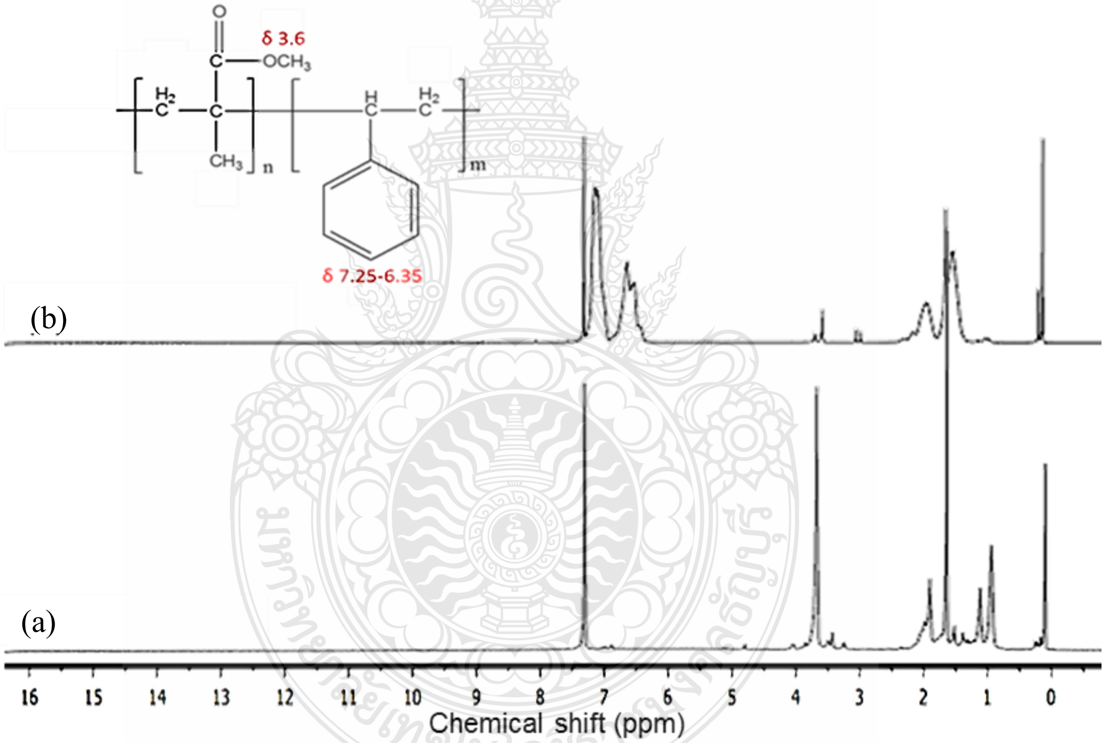


**Figure 4.21** $^1$H NMR spectra of PMMA-I (a) after methylation with TMSD prepared by solution and PMAA-*b*-PS (b) prepared by emulsion ITP using purified PMAA-I at 60 °C under pH~9 (with KOH) at final conversion

From the results in this part, it concluded that the spherical with high stable PMMA-*b*-PS particles without coagulation was prepared by emulsion ITP using purified PMAA-I as a macro chain transfer agent. In addition, a much smaller particle with quite narrower particle size distribution was obtained using purified than unpurified PMAA-I. Both control and living nature were not different for both conditions. This indicated that the unreacted $CHI_3$ (previously precipitated in aqueous continuous phase) of the unpurified PMAA-I condition diffused into the formed particles may lose activity. The precipitated $CHI_3$ existed in the aqueous for a long period may the reason of performance depression. Moreover, $M_w/M_n$ of about 2 was still quite high and needed to improve. Therefore, post addition of $CHI_3$ into emulsion ITP with a short period dispersed in the aqueous medium of $CHI_3$ would the possible method to reduce MWD of PMMA-*b*-PS.

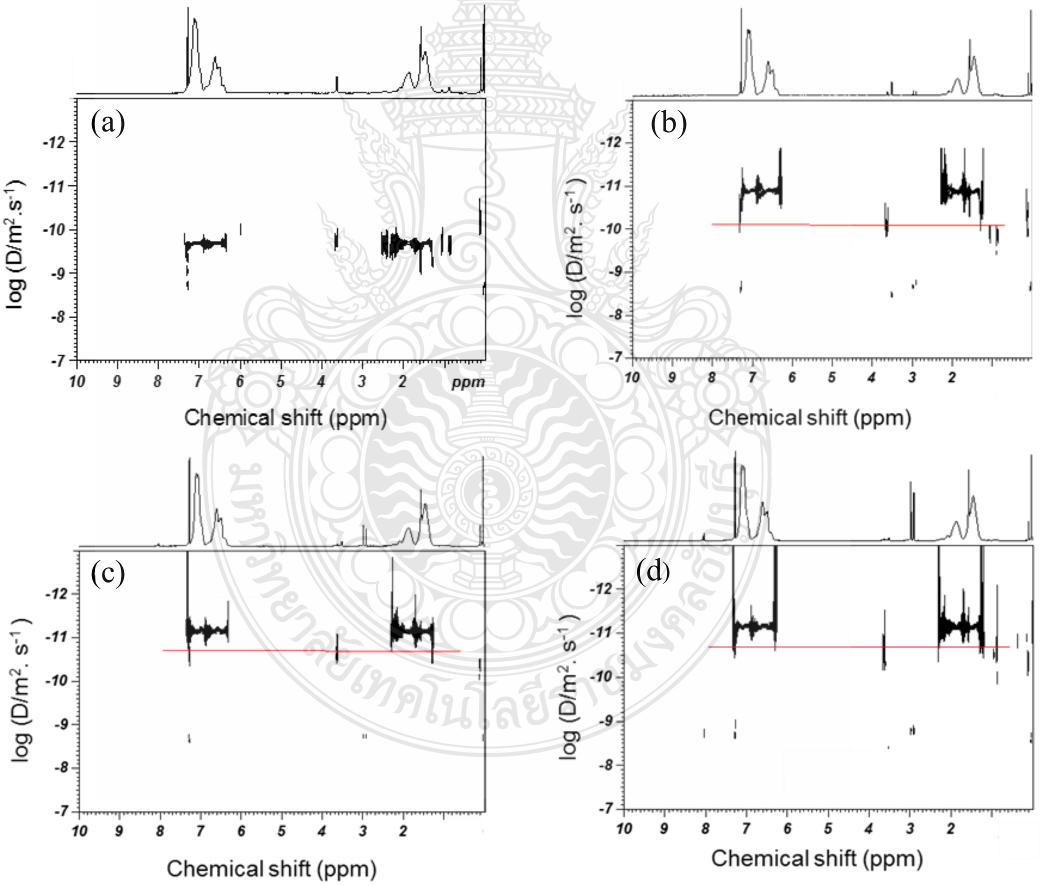


**Figure 4.22** DOSY NMR spectra of PMAA-*b*-PS (after methylation with TMSD) spectra prepared by emulsion ITP at various conversions (%) : 11 (a) 32 (b), 92 (c) and 93 (d)

### 4.2.3 Influence of the post addition of $CH_3$ solution after polymerization at various times

In the previous part, approximately 64% of $CHI_3$ did not participate in the emulsion ITP as PMAA-I macro chain transfer agents although they post-diffused into the formed particles. The controlling nature was clearly shown that most of $CHI_3$ diffused into the formed particles were lose activity. In this part, the fresh $CHI_3$ with the equality amount of 64% left (0.43 mmol) in the purified process of PMAA-I was additionally posted in the emulsion ITP where the purified PMAA-I was used as a macro chain transfer agent. Various additional times as 30, 60 and 90 mins of the fresh $CHI_3$ were studied.

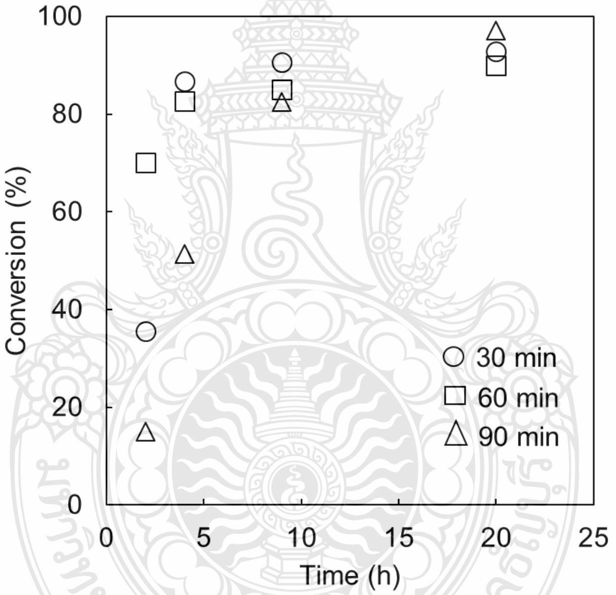


**Figure 4.23** Conversion versus time plots of PMAA-*b*-PS prepared by emulsion ITP using purified PMAA-I macro chain transfer agent and V-501 initiator at 60°C pH~9 (with KOH) with various times as 30, 60 and 90 mins at addition of $CHI_3$ the after polymerization at using styrene/PMAA-I/ V-501(molar ratio) = 400/1/1

Emulsion ITP of three conditions smoothly proceeded as shown in Fig. 4.23. The polymerizations reached to high conversion (%) within 24 h. The polymerization rates were not different. This indicated that the additional time of $CHI_3$ seemed less effect on the polymerization rate. However, the control and living nature of the obtained PMMA-*b*-PS particles may somewhat different with various additional time of $CHI_3$. The control and living nature of the obtained PMMA-*b*-PS particles in terms of $M_n$ and $M_w/M_n$ were shown in Table 4.7.

**Table 4.7** The $M_n$ and $M_w/M_n$ of PMAA-*b*-PS (after methylation) obtained by emulsion ITP using purified PMAA-I macro chain transfer agent and V-501 as an initiator at pH~9 (with KOH) with the various times (30, 60 and 90 min) addition of $CHI_3$ after polymerization at) at each conversion

| **Additional time (min)** | **Time (h)** | **Conversion (%)** | $M_{n, th}$ | $M_{n,exp}$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 30 | 2 | 36 | 83,00 | 125,400 | 2.53 |
| | 4 | 87 | 16,300 | 212,500 | 2.26 |
| | 9 | 91 | 16,900 | 236,200 | 2.34 |
| | 20 | 93 | 17,200 | 236,300 | 2.39 |
| 60 | 2 | 70 | 13,800 | 179,800 | 2.07 |
| | 4 | 83 | 15,700 | 201,700 | 2.10 |
| | 9 | 85 | 16,100 | 213,100 | 2.09 |
| | 20 | 90 | 16,900 | 231,500 | 2.02 |
| 90 | 2 | 15 | 5,100 | 87,600 | 2.27 |
| | 4 | 51 | 10,700 | 137,400 | 2.02 |
| | 9 | 82 | 15,500 | 220,100 | 1.86 |
| | 20 | 97 | 17,700 | 247,400 | 1.84 |

For all conditions, the $M_n$ of the obtained PMAA-*b*-PS is almost the same throughout the polymerization. In addition, $M_n$ increased with the conversion and they were significantly higher than the theoretical $M_n$. The MWDs with a monomodal distribution curve shifted to higher molecular weight with an increase of conversion (Fig. 4.24). These indicated that PMAA-*b*-PS prepared by three conditions maintained living nature.

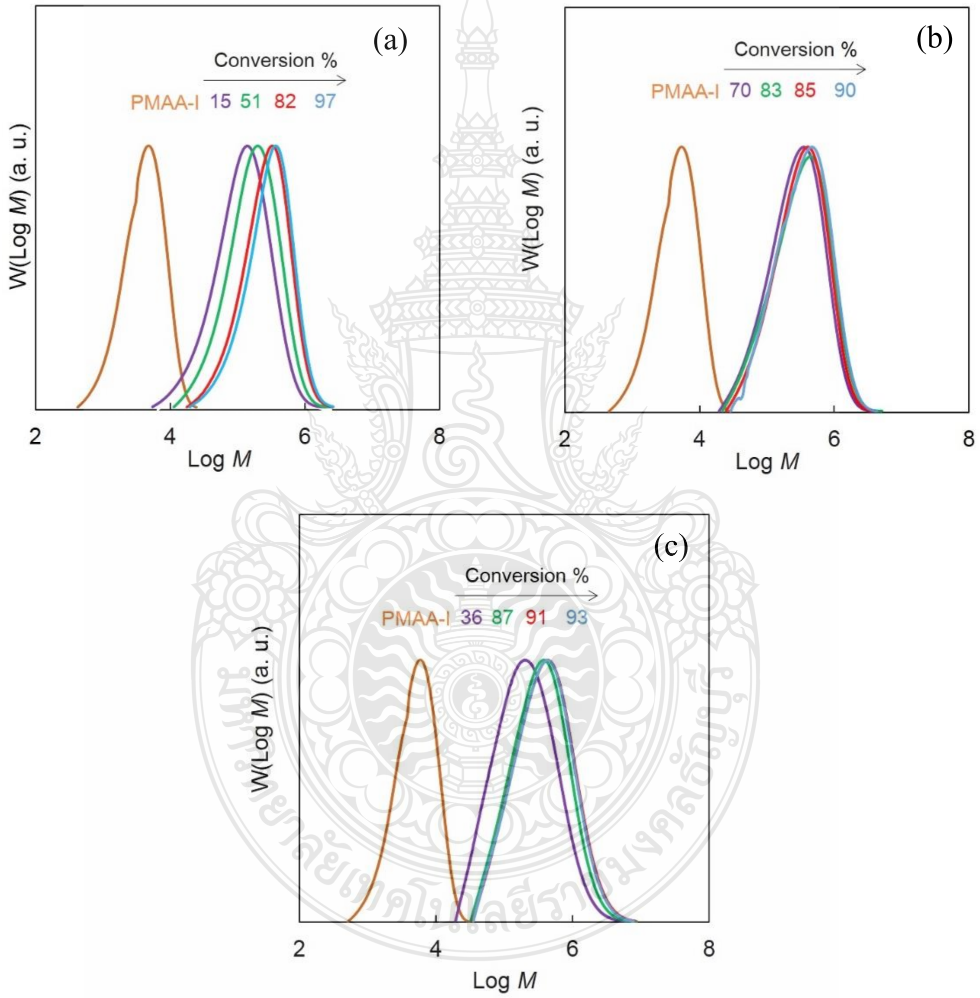


**Figure 4.24** MWDs of PMMA-*b*-PS (after methylation TMSD) prepared by emulsion ITP using purified PMAA-I macro chain transfer agent and V-501 initiator under 60 °C at pH~9 (with KOH) with the addition of $CHI_3$ after polymerization at various time (min): 30 (a), 60 (b) and 90 (c) using styrene/PMAA-I/V-501(molar ratio) = 400/1/1

As seen in Fig. 4.25, the $M_w/M_n$ values (~2.3) of the obtained PMMA-*b*-PS of the addition of $CHI_3$ at 30 min were not different from those (~2.3) of the absence of the addition of $CHI_3$ (previous part) throughout the polymerization. However, the $M_w/M_n$ was improved with an increase of $CHI_3$ additional time where the $M_w/M_n$ values of PMMA-*b*-PS at the final conversion were approximately 2.02 and 1.84 for 60 and 90 mins of $CHI_3$ additional time, respectively. At the additional time of 90 min, the polymerization proceeds with the best control manner

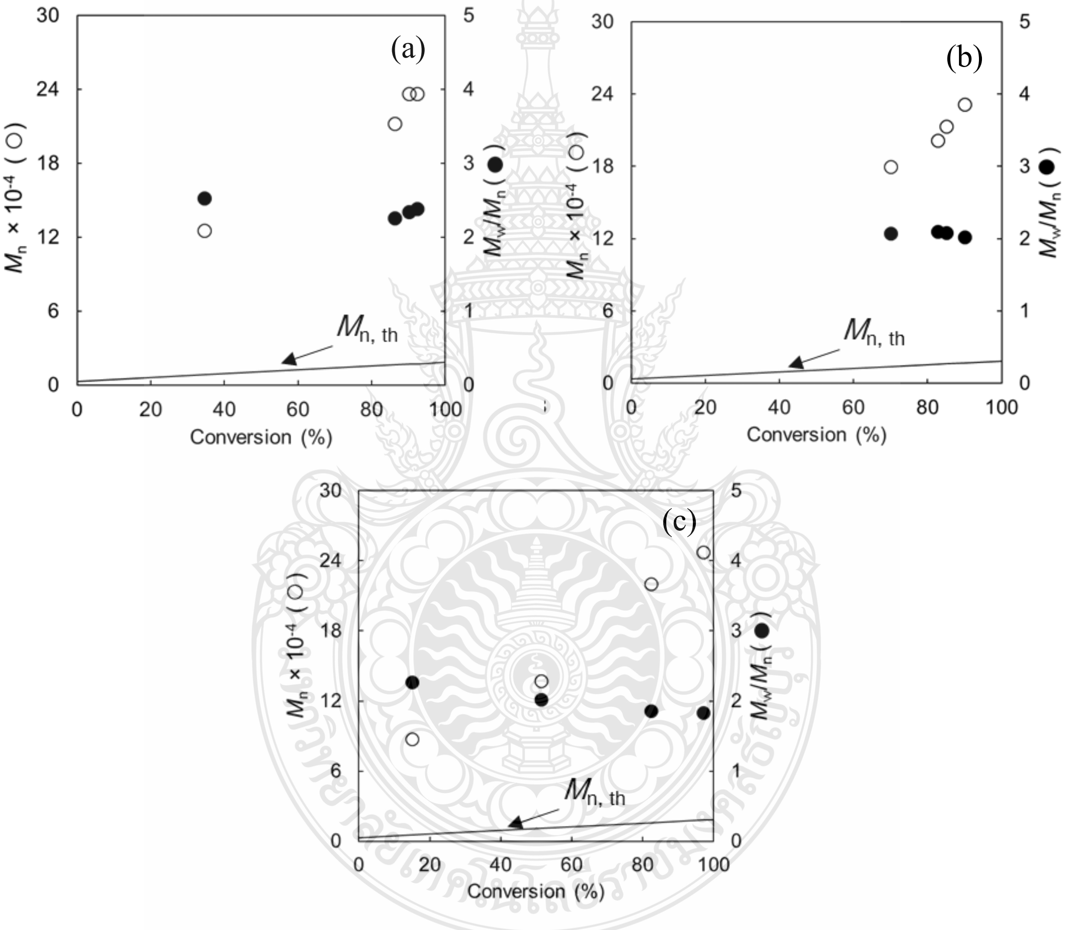


**Figure 4.25** $M_n$ (open circles) and $M_w/M_n$ (closed circles) of PMMA-*b*-PS (after methylation TMSD) prepared by emulsion ITP using purified PMAA-I macro chain transfer agent under 60 °C at pH~9 (with KOH) with the addition of $CHI_3$ after polymerization at various times (min): 30 (a), 60 (b) and 90 (c) using styrene/PMAA-I/V-501(molar ratio) = 400/1/1

For all conditions, the obtained PMAA-*b*-PS particles size were in the range of 120-140 nm (Table 4.7) and increased with the conversion. This indicated that the polymer mainly formed based on the self-assembly of PMAA-*b*-PS chain as discussed in the previous part. In addition, particle size distribution curves represented monomodal distribution for all conditions and throughout the polymerization (Fig. 4.26-28). The obtained PMAA-*b*-PS particle represented high colloidal stability without coagulation where the $N_p$ (Table 4.8) was quite constant throughout the polymerization. It is due to a high negative charge (~-50 mV) derived from the carboxyl group of MAA segments as a hairy surface on the polymer particles. They could play the role as a stabilizer to prevent polymer particle aggregation. In addition, the uniform spherical PMAA-*b*-PS with submicrometer-sized were also observed by TEM photographs (Fig. 4.29).

**Table 4.8** Weight- number average diameter ($d_w$ and $d_n$, respectivelty) , size distribution ($d_w/d_n$), zeta potential, and $N_p$ of PMAA-*b*-PS particles obtained by emulsion ITP using purified PMAA-I macro chain transfer agent and V-501 as an initiator at pH~9 (with KOH) with at various times (30, 60 and 90 min) of the addition of $CHI_3$ after polymerization at each conversion

| **Additional time (min)** | **Time (h)** | **Conversion (%)** | $d_n$ **(nm)** | $d_w / d_n$ | $N_p \times 10^{16}$ $(L^{-1})$ | **Zeta potential (mV)** |
|---|---|---|---|---|---|---|
| 30 | 2 | 36 | 94 | 1.1 | 9.0 | - |
| | 4 | 87 | 106 | 1.2 | 13.1 | - |
| | 9 | 91 | 118 | 1.1 | 10.2 | - |
| | 20 | 93 | 122 | 1.1 | 9.6 | -51 |
| 60 | 2 | 70 | 108 | 1.1 | 10.5 | - |
| | 4 | 83 | 109 | 1.1 | 12.1 | - |
| | 9 | 85 | 118 | 1.1 | 9.8 | - |
| | 20 | 90 | 124 | 1.0 | 9.5 | -48 |
| 90 | 2 | 15 | 72 | 1.2 | 7.5 | - |
| | 4 | 51 | 108 | 1.1 | 7.6 | - |
| | 9 | 82 | 132 | 1.1 | 6.7 | - |
| | 20 | 97 | 146 | 1.1 | 5.9 | -53 |

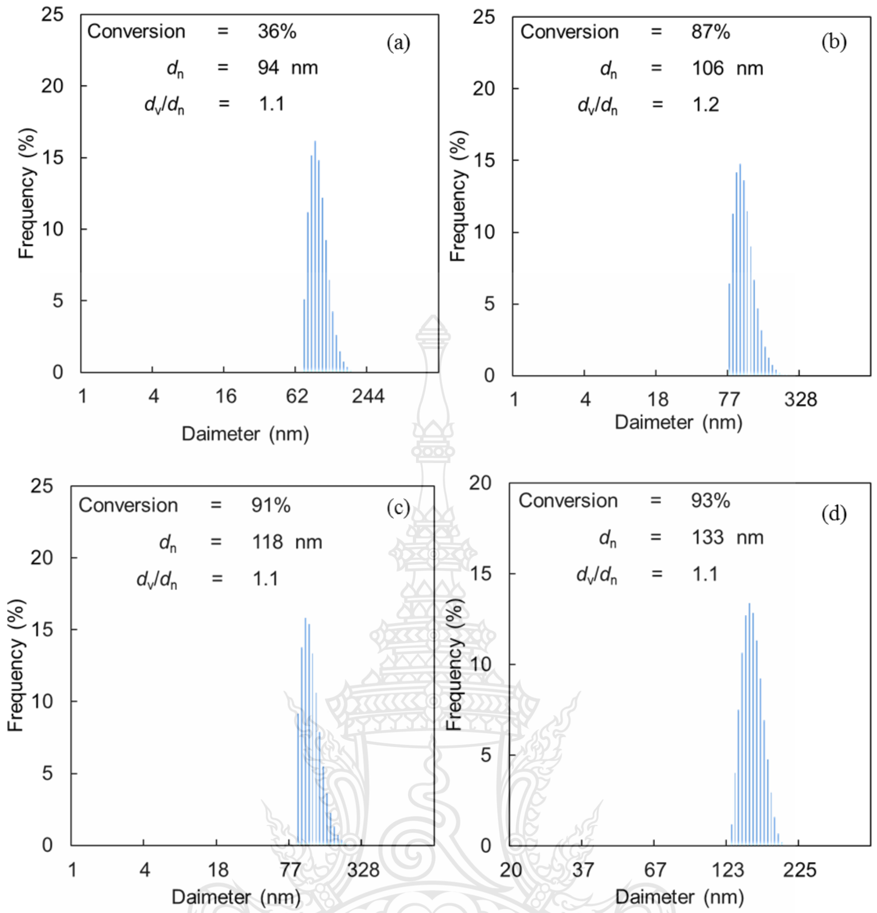


**Figure 4.26** Size distributions (number distribution; measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP using purified PMAA-I macro chain transfer agent under and V-501 initiator at 60 °C under pH~9 (with KOH) with the addition of $CH_3$ after polymerization at 30 min at various conversions (%): 36 (a), 87(b), 91 (c), and 93 (d)

From the results, it was found that various additional times of $CHI_3$ did not any affect the living nature, particle size, particle shape and colloidal stability of the obtained PMAA-*b*-PS particles. By contrast, it did affect to control nature and polymerization rate as well. Here, these phenomena were clearly clarified. It is well known that the polymerization rate ($R_p$) in emulsion polymerization was not only based on monomer concentration but also on a number of particles ($N_p$). At an early stage of the polymerization (2 h) after the addition of $CHI_3$, $R_p$ of both 30 and 60 mins of the additional $CHI_3$ were quite higher than that of 90 min (Fig. 4.23). Although, the later stage of the polymerization was not different. In fact, the R$_p$ between CLRP and CRP was not different even the addition rate of monomer into the polymerizing chain in CRP was significantly higher than that in CLRP. It is due to a much larger number of polymerizing chain (living nature) obtaining in CLRP than CRP. At 2 h of the polymerization, the number of polymerizing chain derived from CHI$_2$ radical and $N_p$ of the additional time of 90 min were lower than those of the faster addition times (30 and 60 min) which resulted in lower $R_p$. The $R_p$ of the 90 min reached to those of the 30 and 60 min in the later stage when most of CHI$_3$ generated CHI$_2$ radical as same as in 30 and 60 min.

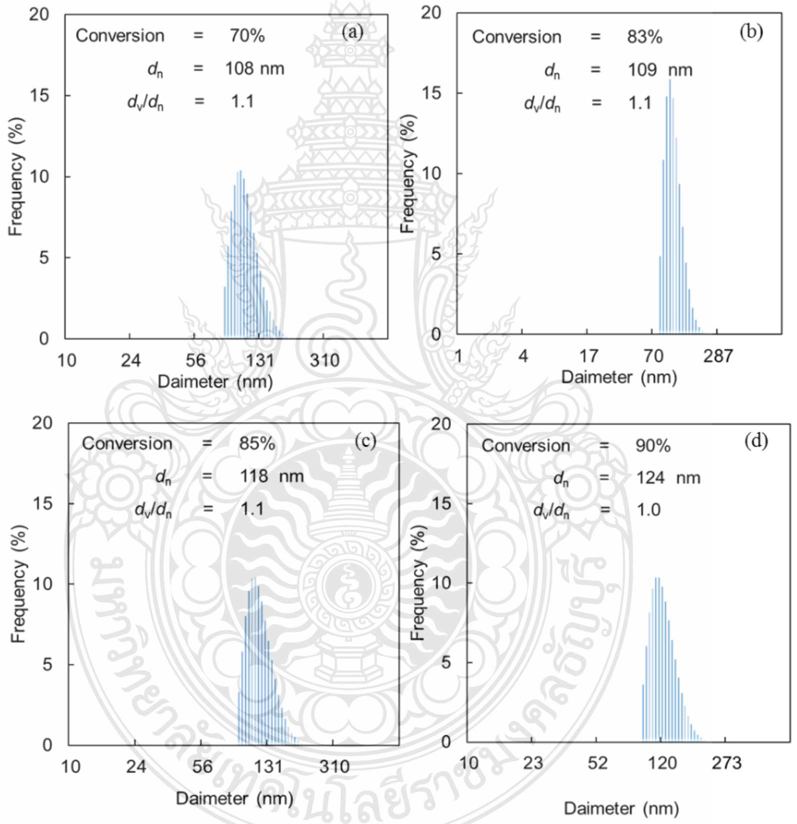


**Figure 4.27** Size distributions (number distribution; measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP using purified PMAA-I macro chain transfer agent under and V-501 initiator at 60 °C underpH~9 (with KOH) with the addition of CH$_3$ after polymerization 60 min at various conversions (%): 70 (a), 83(b), 85 (c) and 90 (d)

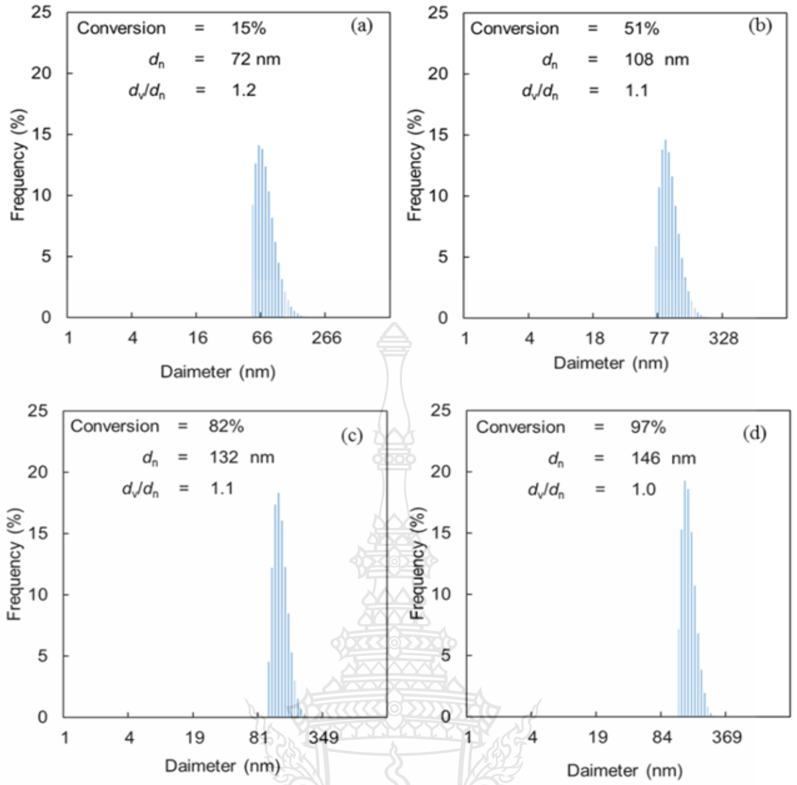


**Figure 4.28** Size distributions (number distribution; measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP using purified PMAA-I macro chain transfer agent under and V-501 initiator at 60 °C under pH~9 (with KOH) with the addition of $CH_3$ after polymerization 90 min at various conversions (%): 15 (a), 51 (b), 82 (c) and 97 (d)

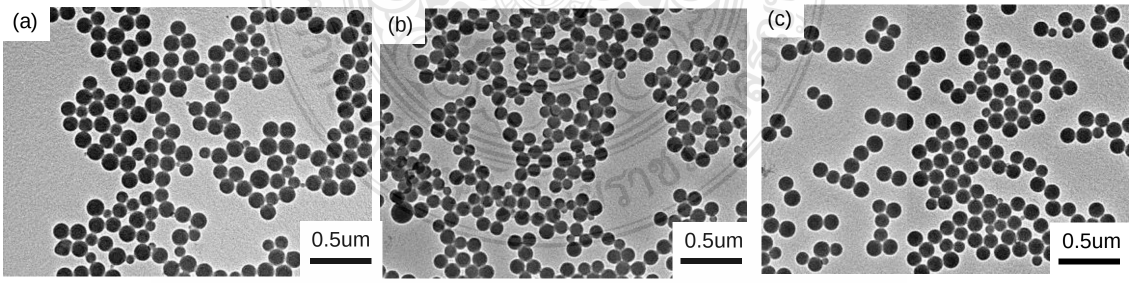


**Figure 4.29** TEM photographs of PMAA-*b*-PS particles (final conversion) prepared by emulsion ITP using purified PMAA-I macro chain transfer agent and V-501 initiator at 60 ºC at pH~9 (with KOH) with the addition of $CH_3$after polymerization at various times (min): 30 (a), 60 (b) and 90 (c)

The reason why the control manner as $M_w/M_n$ of the obtained PMAA-$b$-PS of the $CHI_3$ additional time of 90 min quite lower than the other conditions was explained as a following. Normally, emulsion polymerization divided into three stages as particle formation, particle growth and monomer consumption in the particle. The $N_p$ would be increased throughout the stage one which resulted in an increase of Rp. The polymerization rate was then stable after finishing the first stage as the $N_p$ was constant. The $M_w/M_n$ value was then influenced by the additional time of $CHI_3$. If the $N_p$ existed in the emulsion system was not enough, some of $CHI_3$ added in the continuous aqueous phase then precipitated out which reduced the control performance of emulsion ITP. Therefore, the $N_p$ of PMAA-$b$-PS prepared by emulsion ITP using purified PMAA-I was calculated throughout the polymerization as shown in Fig. 4.30. It was found that a large amount (~14 x $10^{-18}$ $l^{-1}$) of PMAA-$b$-PS particle formed by self-assembly by 30 min and then immediately aggregated as found approximately 5 x $10^{-18}$ $l^{-1}$ of $N_p$ at 60 min. However, $N_p$ again increased and was constant after 90 min. In the early stage of emulsion polymerization, a large amount of the pre-particle was formed and then grown up. Based on high interfacial tension between particle surface (with low anionic hairy layer) and water, the particle then aggregated to be a larger size (decreasing of $N_p$) for the reduction of interfacial tension. In the same time, the generation of the new particle by self-assembly of PMAA-$b$-PS chains still proceeded. When the particle aggregation and formation rates were balanced, the $N$p (~12 x $10^{-18}$ $l^{-1}$) then was constant at about 90 min where most of the growing PMAA-$b$-PS particles maintained their colloidal stability. Based on this result, at 30 and 60 mins of the additional $CHI_3$, the total surface area of PMAA-$b$-PS particles was not enough for $CHI_3$ existed in an aqueous continuous phase. Some of $CHI_3$ then precipitated. On the other hand, a lower amount of $CHI_3$ suddenly partitioned into the polymerizing particles which resulted in low control of the polymerization. By contrast, at 90 min where the induction period of the particle formation was passed, the total surface area of the PMAA-$b$-PS particles was enough to entrap the additional $CHI_3$. The $M_w/M_n$ value (1.84 at the final conversion) was then improved.

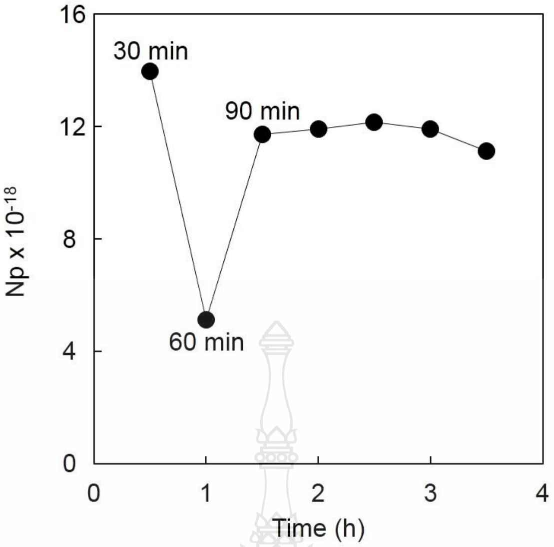


**Figure 4.30** $N_p$ of PMAA-*b*-PS versus time plots of the prepared by emulsion ITP using purified PMAA-I as a macro chain transfer agent, and V-501 as an initiator at 60 ºC

Although $M_w/M_n$ was improved about 1.84, it was still quite far from the ideal ($M_w/M_n = 1$) of control manner. Moreover, $M_{n,\mathrm{exp}}$ value was also still much higher than $M_{n,\mathrm{th.}}$ To improve such values, various amounts of the additional $CHI_3$ was investigated in the next part with the optimal condition using purified PMAA-I as a macro chain transfer agent with the addition of $CH_3$ after polymerization at 90 min.

### 4.2.4. Influence of additional amount of $CHI_3$ in emulsion ITP using purified PMAA-I on the control manner of the obtained PMAA-*b*-PS

In the previous part, the uniform and stable PMAA-*b*-PS particles with submicrometer-sized was successfully prepared by emulsion ITP using purified PMAA-I as a macro chain transfer agent with the addition of $CHI_3$ after a polymerization time of 90 min. In addition, the polymerization proceeded with living nature as the molecular weight increase with the conversion. However, the $M_w/M_n$ (1.84) of the obtained PMAA-*b*-PS particles still needed to be improved. Therefore, various amounts of $CHI_3$ such as

0.43, 0.86 and 1.71 mmol were added into the emulsion ITP after an induction period (90 min). For all contents of $CHI_3$, the polymerization rate was not different where the polymerization reached to the high conversion by 10 h as shown in Fig. 4.31.

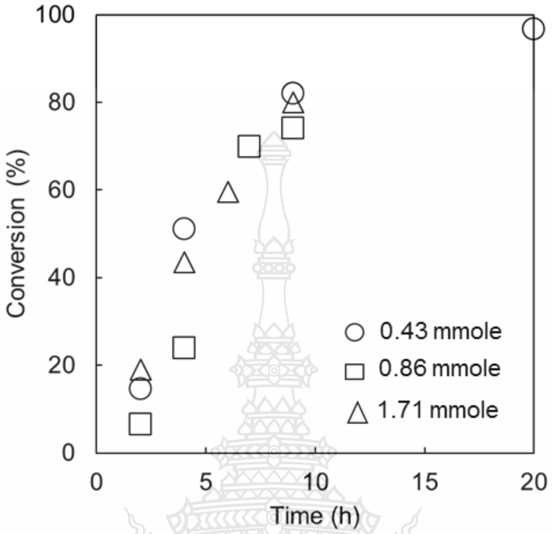


**Figure 4.31** Conversion versus time plots of PMAA-*b*-PS prepared by emulsion ITP using purified PMAA-I as a macro chain transfer agent and V-501 as an initiator at 60 °C at pH~9 (with KOH) with the addition of $CHI_3$ after a polymerization time of 90 min using the various amounts of $CHI_3$ (mmol ): 0.43 (open circle), 0.86 (open square) and 1.71 (open triangle) at using styrene/PMAA-I/V-501(molar ratio) = 400/1/1

As the results are shown in Table 4.9, for three amounts of $CHI_3$, the size of PMAA-*b*-PS particles increased with the conversion without any coagulation. The obtained PMAA-*b*-PS particles represented high colloidal stability where high anionic charge (~-50 mV) from MAA segment anchored on the particle surface as a hair layer. The particle size distribution curves measured by DLS (Figure 4.32-33) also confirmed the explained above that only monomodal distribution curves for all conditions and conversions were observed. In addition, the particle size distribution seemed to represent a uniformed particle where the $d_w/d_n$ values of the obtained PMAA-*b*-PS particles closed to 1 for all conditions. It was similar to the previous part, the spherical PMAA-*b*-PS particle with a submicrometer-sized was obtained (Figure 4.34).

**Table 4.9** Weight ($d_w$) - and number ($d_n$)- average diameter, size distribution ($d_w/d_n$) and zeta potential of PMAA-*b*-PS particles obtained by emulsion ITP using purified PMAA-I and V-501 initiator at pH~9 (with KOH) with various amounts of $CHI_3$ added after a polymerization time of 90 min

| **$CH_3$ content (mmol)** | **Time (h)** | **Conversion (%)** | **$d_w$ (nm)** | **$d_n$ (nm)** | **$d_w$ / $d_n$** | **Zeta potential (mV)** |
|---|---|---|---|---|---|---|
| 0.43 | 2 | 15 | 88 | 72 | 1.2 | - |
| | 4 | 51 | 124 | 108 | 1.1 | - |
| | 9 | 82 | 145 | 132 | 1.1 | - |
| | 20 | 97 | 157 | 146 | 1.1 | -53 |
| 0.86 | 2 | 13 | 66 | 55 | 1.2 | - |
| | 4 | 30 | 86 | 71 | 1.2 | - |
| | 7 | 76 | 131 | 116 | 1.1 | - |
| | 9 | 80 | 136 | 124 | 1.1 | -48 |
| 1.71 | 2 | 19 | 87 | 69 | 1.3 | - |
| | 4 | 44 | 128 | 113 | 1.1 | - |
| | 6 | 60 | 146 | 131 | 1.1 | - |
| | 9 | 80 | 161 | 147 | 1.1 | -52 |

For three amounts of $CHI_3$ added into the emulsion system after 90 min, the $M_{n,\,exp}$ increased with conversion as shown in Table 4.10. In addition, the MWDs shifted to higher molecular weight with increasing conversion (Figure 4.35) which indicated the living nature of polymer obtained from all conditions. The $M_n$ with all conversions of the obtained PMAA-*b*-PS seemed a bit decrease and an approach the theoretical $M_n$ with the additional amount of $CHI_3$. In addition, the increase of $CHI_3$ effectively decreased the $M_w/M_n$ in which at the final conversion it was 1.84, 1.46 and 1.24 for $CHI_3$ amount of 0.43, 0.86 and 1.71 mmol, respectively.

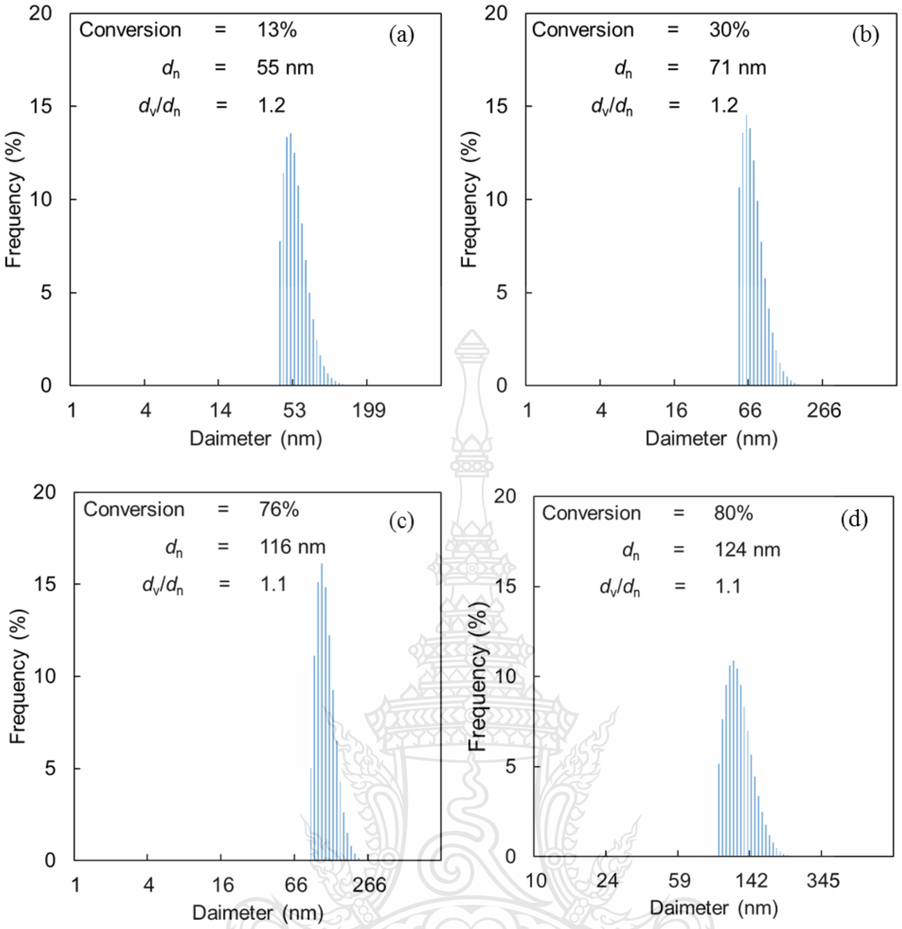


**Figure 4.32** Size distributions (number distribution; measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP using purified PMAA-I macro chain transfer agent and V-501 initiator at 60 °C under pH~9 (with KOH) with the addition of $CH_3$ (0.86 mmol) after polymerization 90 min at various conversions (%):13 (a), 30 (b), 76 (c) and 80 (d)

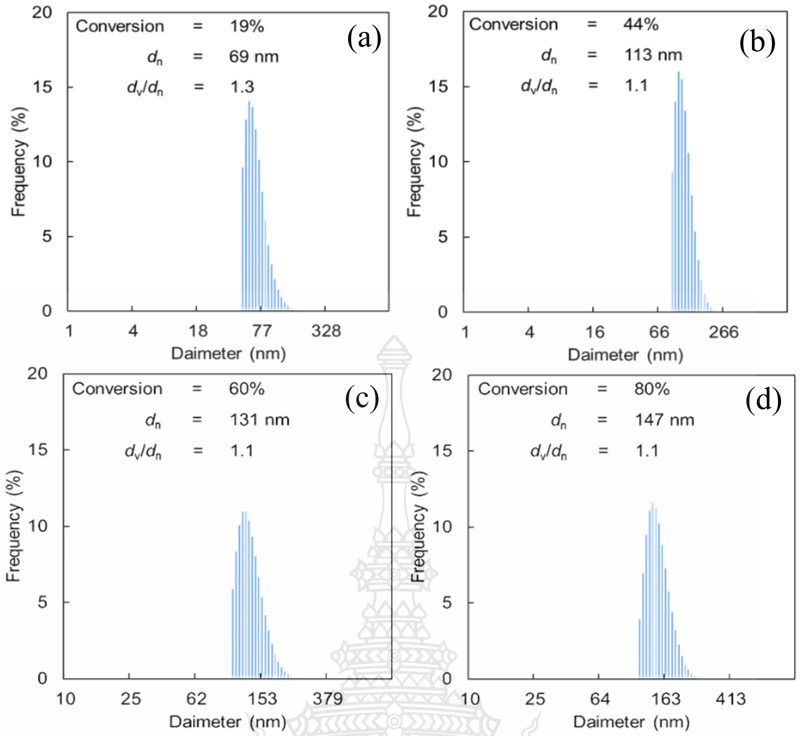


**Figure 4.33** Size distributions (number distribution; measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP using purified PMAA-I macro chain transfer agent and V-501 initiator at 60 °C under pH~9 with the addition of $CH_3$ (1.71 mmol) after polymerization 90 min at various conversions (%):19 (a), 44 (b), 60 (c) and 80 (d)

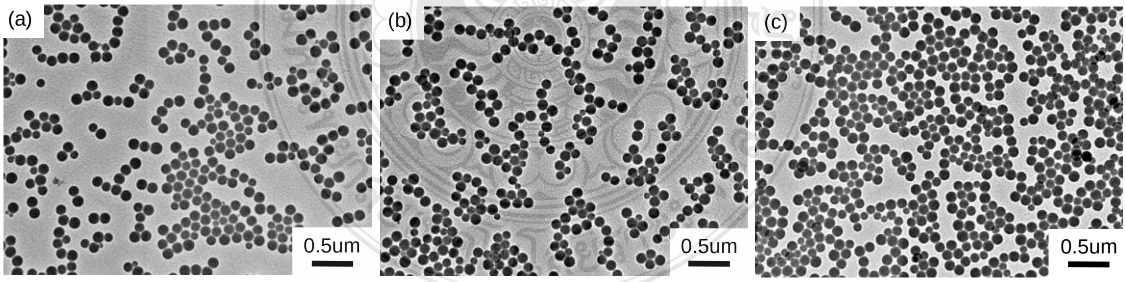


**Figure 4.34** TEM photographs of PMAA-*b*-PS particles (final conversion) by emulsion ITP using purified PMAA-I as a macro chain transfer agent and V-501 initiator under 60 °C at pH~9 (with KOH) with the addition of $CHI_3$ after polymerization of 90 min with various amounts of $CHI_3$ (mmol): 0.43 (a), 0.86 (b) and 1.71 (c)

**Table 4.10** The $M_n$ and $M_w/M_n$ of PMAA-*b*-PS (after methylation) obtained by emulsion ITP using purified PMAA-I macro chain transfer agent and V-501 initiator at pH~9 (with KOH) with various amounts of $CHI_3$ added after a polymerization time of 90 min

| $CHI_3$ content (mmol) | Time (h) | Conversion (%) | $M_{n, th}$ | $M_{n, exp}$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 0.43 | 2 | 15 | 5,100 | 87,600 | 2.27 |
| | 4 | 51 | 10,700 | 137,400 | 2.02 |
| | 9 | 82 | 15,500 | 220,100 | 1.86 |
| | 20 | 97 | 17,700 | 247,400 | 1.84 |
| 0.86 | 2 | 13 | 4,100 | 6,400 | 1.31 |
| | | | - | 69,600 | 1.43 |
| | 4 | 30 | 5,700 | 16,000 | 1.40 |
| | 7 | 76 | 10,000 | 34,300 | 1.42 |
| | 9 | 80 | 10,400 | 37,400 | 1.46 |
| 1.71 | 2 | 19 | 3,900 | 3,500 | 1.49 |
| | | | - | 69,000 | 1.36 |
| | 4 | 44 | 5,200 | 11,300 | 1.19 |
| | 7 | 60 | 6,000 | 15,100 | 1.24 |
| | 9 | 80 | 7,000 | 20,100 | 1.24 |

However, at 13% (Fig.4.35 (b)) and 19% (Fig. 4.35 (c)) conversions, respectively, of 0.86 and 1.71 mmol of $CHI_3$ added, the bimodal MWD curves were observed. In both cases, $M_n$ of the larger peak (6,400 and 3,500 g/mol for 0.86 and 1.71 mmol of $CHI_3$ added, respectively ) was closed to the theoretical $M_n$ (4,100 and 3,900 g/mol for 0.86 and 1.71 mmol of $CHI_3$ added, respectively). On the other hand, $M_n$ of the smaller peak was approximately 69,000 g/mol for both cases. Moreover, the $M_n$ of later peaks accorded with the $M_n$ at a similar conversion obtained from the conditions with (0.43 mmol) and without the addition of $CHI_3$. This indicated that a lower amount of iodine radical as a chain transfer agent existed in the systems of both with 0.43 mmol and without $CHI_3$. Thus, the rate of termination was high which resulted in higher $M_n$ and MWD. The main polymer chain in the formed particle would be PMAA-*b*-PS. Similarly, at the low conversion of both 0.86 and 1.71 mmol of $CHI_3$ added, the main polymerization was based on the growing PMAA-*b*-PS chain. However, after $CHI_3$ was added and diffused into the polymerizing particle where a large amount of $CHI_3$ participated in the polymerization in the particle, a number of CHI2-PS chain derived from $CHI_2$ • was polymerized competition with the block copolymer chain. After several minutes, $CHI_2$-PS chains became the main polymerization where the larger peak of the much lower Mn was observed in both 0.86 and 1.71 mmol of CHI3 added conditions. Thereafter, the larger Mn peak disappeared at the higher conversion. Based on a larger amount of $CHI_3$ participated in the polymerization, the control manner was significantly improved as MWD at the final conversion decreased from 1.84 to 1.24 for 0.43 mmol to 1.71 mmol of $CHI_3$ added, respectively.

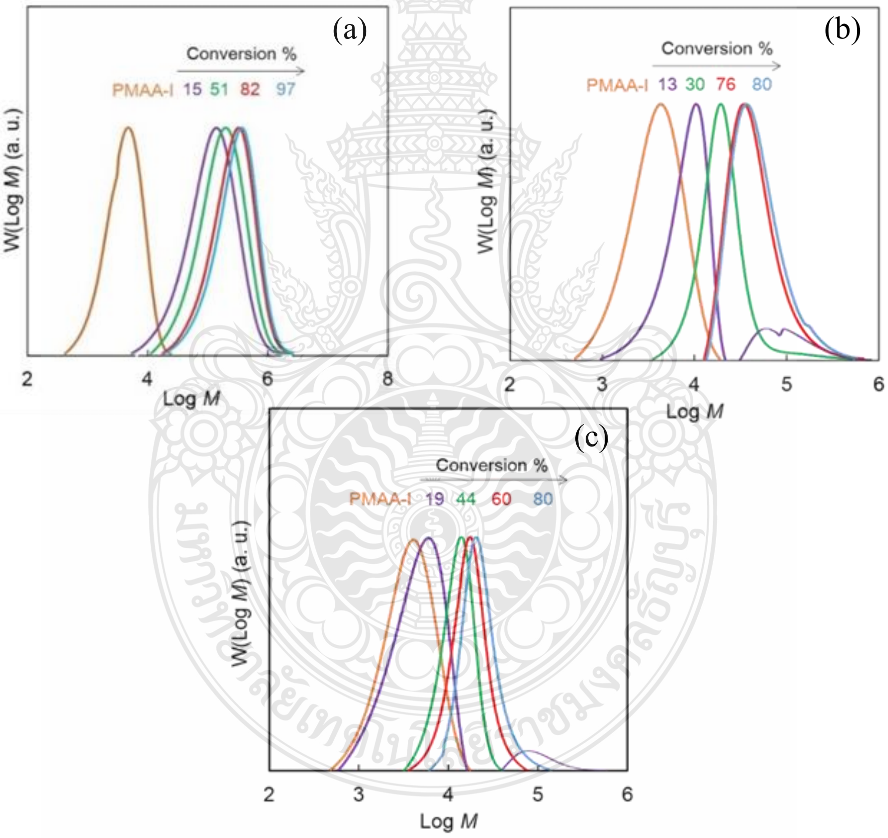


**Figure 4.35** MWDs of PMMA-*b*-PS (after methylation TMSD) prepared by emulsion ITP using purified PMAA-I as a macro chain transfer agent and V-501 initiator under 60 °C atpH~9 (with KOH) with the addition of CHI3 after polymerization at 90 min with various amounts of $CHI_3$ (mmol): 0.43 (a), 0.86 (b) and 1.71 (c) using styrene/PMAA-I/V-501(molar ratio) = 400/1/1

# CHAPTER 5

# CONCLUSIONS

This research was purposed to study the preparation of PMAA-*b*-PS particles by emulsion ITP using PMAA-I as a macro chain transfer agent and stabilizer where the particle formation was formed based on the self-assembly mechanism of PMAA-*b*-PS chains. To obtain the uniform and stable PMAA-*b*-PS particle with good control and livingness, various parameters were studied as a following.

The first part, PMAA-I as a macro chain transfer agent was synthesized by both solution ITP and RTCP. For both conditions, the polymerizations smoothly proceeded and the monomer conversion attained at 100% by 24 h. The $M_n$ (3,400 and 3,800 g/mol for solution ITP and RTCP, respectively) and $M_w/M_n$ (1.60 and 1.66 for solution ITP and RTCP, respectively) of the obtained PMAA-I prepared by both techniques were not different. To avoid using a large amount of chemical compound, solution ITP was selected to produce the PMAA-I for emulsion ITP in the further part. The second part, emulsion ITP of PMAA-*b*-PS particles using PMAA-I as a macro chain transfer agent and a stabilizer to obtain good control and livingness and also to maintain the colloidal stability of polymer particles. In this part, the influence of the aqueous continuous phase pH as acidic (pH~4) and alkaline (pH~9) pH conditions on the particle formation and the colloidal stability of the obtained PMAA-*b*-PS particles was studied. It was found that emulsion ITP in the alkaline condition represented more high performance than in acidic condition. The uniform and stable PMAA-*b*-PS particle with living nature as experimental $M_n$ closed to theoretical $M_n$ were obtained. The polymerization smoothly proceeded and reached 100% conversion without any particle coagulation. The spherical PMAA-*b*-PS particles with a submicrometer-sized of 223 nm were obtained which indicated that the particle was formed based on self-assembly mechanism. However, the $M_w/M_n$ value (~2.1) of the obtained PMAA-*b*-PS was still quite high. It was due to some $CHI_3$ in solution ITP system did not participate in emulsion ITP. They precipitated in alkaline aqueous continuous phase after PMAA-I solution was added into the emulsion ITP system. Although they later diffused into the formed particle, most of them were loss activity as the obtained $M_w/M_n$ was not evidently improved from using only purified

PMAA-I (~ 2.2). To improve this value, $CHI_3$ (0.42 mmol) was added at various times into the emulsion ITP system using purified PMAA-I at the alkaline condition. At 90 min after polymerization, the $M_w/M_n$ of the obtained PMAA-*b*-PS particles was improved where it was 1.84 at the final conversion. It was due to all pre-particles were formed in the system where $CHI_3$ added was quickly diffused into the particle to participate in the polymerization without losing activity. However, the experimental $M_n$ was much higher than the theoretical one because the polymer chain was quite low in the system. To increase such polymer chain, various amounts of $CHI_3$ later presenting $CHI_2\bullet$ were then added into the emulsion ITP system. The $M_w/M_n$ value (1.24) was significantly reduced with 1.71 mmol of $CHI_3$. The number of polymer chain was increased with $CHI_2\bullet$. On the other hand, the obtained polymer particle contained both PMAA-*b*-PS and PS chains. The PMAA-*b*-PS chain initiated from self-assembly of the particle in the aqueous phase and continued extent in the formed particle whereas PS chain was later formed with $CHI_2\bullet$ inside the particle after incoming of $CHI_3$.

From all results, it can conclude that the uniform and stable spherical PMAA-*b*-PS particles with good colloidal stability are successfully prepared by emulsion ITP for the first time using purified PMAA-I as a macro chain transfer agent with post addition of $CHI_3$. Moreover, the PMAA-*b*-PS particle represented a narrow MWD with good living nature.

# List of Bibliography

[1] V. I. Eliseeva, S. Ivanchev, S. Kuchanov, and A. Lebedev, *Emulsion polymerization and its applications in industry*: Springer Science & Business Media, 2012.

[2] M. A. Villalobos and J. Debling, "Bulk and Solution Processes," *Handbook of Polymer Synthesis, Characterization, and Processing,* pp. 273-294, 2013.

[3] G. Odian, *Principles of polymerization*: John Wiley & Sons, 2004.

[4] E. Saldivar-Guerra and E. Vivaldo-Lima, *Handbook of polymer synthesis, characterization, and processing*: John Wiley & Sons, 2013.

[5] K. Matyjaszewski and T. P. Davis, *Handbook of radical polymerization*: Wiley Online Library, 2002.

[6] K. Matyjaszewski, *Advances in controlled/living radical polymerization*: American Chemical Society; Distributed by Oxford University Press, 2003.

[7] W. A. Braunecker and K. Matyjaszewski, "Controlled/living radical polymerization: features, developments, and perspectives," *Progress in Polymer Science,* vol. 32, pp. 93-146, 2007.

[8] C. J. Hawker, A. W. Bosman, and E. Harth, "New polymer synthesis by nitroxide mediated living radical polymerizations," *Chemical reviews,* vol. 101, pp. 3661-3688, 2001.

[9] J. Nicolas, Y. Guillaneuf, C. Lefay, D. Bertin, D. Gigmes, and B. Charleux, "Nitroxide-mediated polymerization," *Progress in Polymer Science,* vol. 38, pp. 63-235, 2013.

[10] A. Studer and T. Schulte, "Nitroxide-mediated radical processes," *The Chemical Record,* vol. 5, pp. 27-35, 2005.

## List of Bibliography (continued)

[11] J.-S. Wang and K. Matyjaszewski, "Controlled/" living" radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes," *Journal of the American Chemical Society,* vol. 117, pp. 5614-5615, 1995.

[12] K. Matyjaszewski and J. Xia, "Atom transfer radical polymerization," *Chemical reviews,* vol. 101, pp. 2921-2990, 2001.

[13] J.-S. Wang and K. Matyjaszewski, "Controlled/" living" radical polymerization. Halogen atom transfer radical polymerization promoted by a Cu (I)/Cu (II) redox process," *Macromolecules,* vol. 28, pp. 7901-7910, 1995.

[14] J. Chiefari, Y. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. Le*, et al.*, "Living free-radical polymerization by reversible addition− fragmentation chain transfer: the RAFT process," *Macromolecules,* vol. 31, pp. 5559-5562, 1998.

[15] R. T. Mayadunne, E. Rizzardo, J. Chiefari, Y. K. Chong, G. Moad, and S. H. Thang, "Living radical polymerization with reversible addition− fragmentation chain transfer (RAFT polymerization) using dithiocarbamates as chain transfer agents," *Macromolecules,* vol. 32, pp. 6977-6980, 1999.

[16] S. Perrier and P. Takolpuckdee, "Macromolecular design via reversible addition–fragmentation chain transfer (RAFT)/xanthates (MADIX) polymerization," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 43, pp. 5347-5393, 2005.

[17] G. Moad, E. Rizzardo, and S. H. Thang, "Living radical polymerization by the RAFT process—a first update," *Australian Journal of Chemistry,* vol. 59, pp. 669-692, 2006.

## List of Bibliography (continued)

[18] S. Yamago, K. Iida, and J.-i. Yoshida, "Tailored synthesis of structurally defined polymers by organotellurium-mediated living radical polymerization (TERP): synthesis of poly (meth) acrylate derivatives and their di-and triblock copolymers," *Journal of the American Chemical Society,* vol. 124, pp. 13666-13667, 2002.

[19] S. Yamago, "Development of organotellurium-mediated and organostibine-mediated living radical polymerization reactions," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 44, pp. 1-12, 2006.

[20] S. Yamago, "Precision polymer synthesis by degenerative transfer controlled/living radical polymerization using organotellurium, organostibine, and organobismuthine chain-transfer agents," *Chemical reviews,* vol. 109, pp. 5051-5068, 2009.

[21] S. G. Gaynor, J.-S. Wang, and K. Matyjaszewski, "Controlled radical polymerization by degenerative transfer: effect of the structure of the transfer agent," *Macromolecules,* vol. 28, pp. 8051-8056, 1995.

[22] K. Matyjaszewski, S. Gaynor, and J.-S. Wang, "Controlled radical polymerizations: the use of alkyl iodides in degenerative transfer," *Macromolecules,* vol. 28, pp. 2093-2095, 1995.

[23] C. Boyer, D. Valade, L. Sauguet, B. Ameduri, and B. Boutevin, "Iodine transfer polymerization (ITP) of vinylidene fluoride (VDF). Influence of the defect of VDF chaining on the control of ITP," *Macromolecules,* vol. 38, pp. 10353-10362, 2005.

[24] A. Goto, K. Ohno, and T. Fukuda, "Mechanism and kinetics of iodide-mediated polymerization of styrene," *Macromolecules,* vol. 31, pp. 2809-2814, 1998.

## List of Bibliography (continued)

[25] A. Goto, Y. Tsujii, and T. Fukuda, "Reversible chain transfer catalyzed polymerization (RTCP): A new class of living radical polymerization," *Polymer,* vol. 49, pp. 5177-5185, 2008.

[26] J. Qiu, B. Charleux, and K. Matyjaszewski, "Controlled/living radical polymerization in aqueous media: homogeneous and heterogeneous systems," *Progress in Polymer Science,* vol. 26, pp. 2083-2134, 2001.

[27] K. Robinson, M. Khan, M. de Paz Banez, X. Wang, and S. Armes, "Controlled polymerization of 2-hydroxyethyl methacrylate by ATRP at ambient temperature," *Macromolecules,* vol. 34, pp. 3155-3158, 2001.

[28] R. Mchale, F. Aldabbagh, and P. B. Zetterlund, "The role of excess nitroxide in the SG1 (N-tert-butyl-N-[1-diethylphosphono-(2, 2-dimethylpropyl)] nitroxide)-mediated polymerization of methyl methacrylate," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 45, pp. 2194-2203, 2007.

[29] P. B. Zetterlund, Y. Kagawa, and M. Okubo, "Controlled/living radical polymerization in dispersed systems," *Chemical reviews,* vol. 108, pp. 3747-3794, 2008.

[30] J.-S. Song and M. A. Winnik, "Monodisperse, micron-sized reactive low molar mass polymer microspheres by two-stage living radical dispersion polymerization of styrene," *Macromolecules,* vol. 39, pp. 8318-8325, 2006.

[31] J. D. Biasutti, T. P. Davis, F. P. Lucien, and J. Heuts, "Reversible addition–fragmentation chain transfer polymerization of methyl methacrylate in suspension," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 43, pp. 2001-2012, 2005.

## List of Bibliography (continued)

[32] Y. Sugihara, Y. Kagawa, S. Yamago, and M. Okubo, "Organotellurium-mediated living radical polymerization in miniemulsion," *Macromolecules,* vol. 40, pp. 9208-9211, 2007.

[33] S. Liu, K. D. Hermanson, and E. W. Kaler, "Reversible addition-fragmentation chain transfer polymerization in microemulsion," *Macromolecules,* vol. 39, pp. 4345-4350, 2006.

[34] S. W. Prescott, M. J. Ballard, E. Rizzardo, and R. G. Gilbert, "RAFT in emulsion polymerization: what makes it different?," *Australian journal of chemistry,* vol. 55, pp. 415-424, 2002.

[35] G. Moad, J. Chiefari, Y. K. Chong, J. Krstina, R. T. A. Mayadunne, A. Postma*, et al.*, "Living free radical polymerization with reversible addition–fragmentation chain transfer (the life of RAFT)," *Polymer International,* vol. 49, pp. 993-1001, 2000.

[36] D. Charmot, P. Corpart, H. Adam, S. Zard, T. Biadatti, and G. Bouhadir, "Controlled radical polymerization in dispersed media," in *Macromolecular Symposia*, 2000, pp. 23-32.

[37] C. J. Ferguson, R. J. Hughes, D. Nguyen, B. T. Pham, R. G. Gilbert, A. K. Serelis*, et al.*, "Ab initio emulsion polymerization by RAFT-controlled self-assembly §," *Macromolecules,* vol. 38, pp. 2191-2204, 2005.

[38] C. J. Ferguson, R. J. Hughes, B. T. Pham, B. S. Hawkett, R. G. Gilbert, A. K. Serelis*, et al.*, "Effective ab initio emulsion polymerization under RAFT control," *Macromolecules,* vol. 35, pp. 9243-9245, 2002.

## List of Bibliography (continued)

[39] C. Cheng, J. Shu, S. Gong, L. Shen, Y. Qiao, and C. Fu, "Synthesis and use of a surface-active initiator in emulsion polymerization under AGET and ARGET ATRP conditions," *New Journal of Chemistry,* vol. 34, pp. 163-170, 2010.

[40] J. Shu, C. Cheng, Y. Zheng, L. Shen, Y. Qiao, and C. Fu, "“One pot” synthesis of fluorinated block copolymers using a surface-active ATRP initiator under emulsion polymerization conditions," *Polymer bulletin,* vol. 67, pp. 1185-1200, 2011.

[41] J. Nicolas, B. Charleux, O. Guerret, and S. Magnet, "Nitroxide-mediated controlled free-radical emulsion polymerization using a difunctional water-soluble alkoxyamine initiator. Toward the control of particle size, particle size distribution, and the synthesis of triblock copolymers," *Macromolecules,* vol. 38, pp. 9963-9973, 2005.

[42] E. Groison, S. g. n. Brusseau, F. D’Agosto, S. p. Magnet, R. Inoubli, L. Couvreur*, et al.*, "Well-defined amphiphilic block copolymer nanoobjects via nitroxide-mediated emulsion polymerization," *ACS Macro Letters,* vol. 1, pp. 47-51, 2011.

[43] M. E. Thomson, A.-M. Manley, J. S. Ness, S. C. Schmidt, and M. F. Cunningham, "Nitroxide-mediated surfactant-free emulsion polymerization of n-butyl methacrylate with a small amount of styrene," *Macromolecules,* vol. 43, pp. 7958-7963, 2010.

[44] K. Yan, X. Gao, and Y. Luo, "Well-Defined High Molecular Weight Polystyrene with High Rates and High Livingness Synthesized via Two-Stage RAFT Emulsion Polymerization," *Macromolecular rapid communications,* vol. 36, pp. 1277-1282, 2015.

## List of Bibliography (continued)

[45] J. Rieger, G. Osterwinter, C. Bui, F. Stoffelbach, and B. Charleux, "Surfactant-free controlled/living radical emulsion (co) polymerization of n-butyl acrylate and methyl methacrylate via RAFT using amphiphilic poly (ethylene oxide)-based trithiocarbonate chain transfer agents," *Macromolecules,* vol. 42, pp. 5518-5525, 2009.

[46] I. Chaduc, M. Girod, R. Antoine, B. Charleux, F. D'Agosto, and M. Lansalot, "Batch emulsion polymerization mediated by poly (methacrylic acid) macroRAFT agents: One-pot synthesis of self-stabilized particles," *Macromolecules,* vol. 45, pp. 5881-5893, 2012.

[47] M. Okubo, Y. Sugihara, Y. Kitayama, Y. Kagawa, and H. Minami, "Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization of Butyl Acrylate†," *Macromolecules,* vol. 42, pp. 1979-1984, 2009.

[48] Y. Kitayama, A. Chaiyasat, H. Minami, and M. Okubo, "Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of styrene: polymerization loci," *Macromolecules,* vol. 43, pp. 7465-7471, 2010.

[49] Y. Kitayama, H. Moribe, H. Minami, and M. Okubo, "Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of Styrene: Initial stage of polymerization," *Polymer,* vol. 52, pp. 2729-2734, 2011.

[50] H. Moribe, Y. Kitayama, T. Suzuki, and M. Okubo, "Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of styrene: effect of stirring rate," *Macromolecules,* vol. 44, pp. 263-268, 2010.

[51] Y. Kitayama, H. Moribe, K. Kishida, and M. Okubo, "Emulsifier-free, organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of methyl methacrylate with dimethyl ditelluride as the catalyst," *Polymer Chemistry,* vol. 3, pp. 1555-1559, 2012.

[52] Y. Kitayama, K. Kishida, H. Minami, and M. Okubo, "Preparation of poly (n-butyl acrylate)-b-polystyrene particles by emulsifier-free, organotellurium-mediated living radical emulsion polymerization (emulsion TERP)," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 50, pp. 1991-1996, 2012.

[53] Y. Kitayama, K. Kishida, and M. Okubo, "Emulsifier-free, organotellurium-mediated living radical emulsion polymerization (emulsion TERP): Effect of monomer hydrophilicity," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 51, pp. 716-723, 2013.

[54] J. M. Asua, "Emulsion polymerization: from fundamental mechanisms to process developments," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 42, pp. 1025-1041, 2004.

[55] A. Goto and T. Fukuda, "Kinetics of living radical polymerization," *Progress in Polymer Science,* vol. 29, pp. 329-385, 2004.

[56] T. Otsu and M. Yoshida, "Makromol Chem Rapid Commun 1982, 3, 127," ed: Wiley Online Library| CAS| Web of Science® Times Cited.

[57] C. Le Mercier, S. Acerbis, D. Bertin, F. Chauvin, D. Gigmes, O. Guerret*, et al.*, "Design and use of β-phosphorus nitroxides and alkoxyamines in controlled/"living" free radical polymerizations," in *Macromolecular Symposia*, 2002, pp. 225-247.

[58] H. Fischer, "The persistent radical effect: a principle for selective radical reactions and living radical polymerizations," *Chemical Reviews,* vol. 101, pp. 3581-3610, 2001.

## List of Bibliography (continued)

[59] H. Fischer, "The persistent radical effect in controlled radical polymerizations," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 37, pp. 1885-1901, 1999.

[60] H. Fischer and M. Souaille, "The Persistent Radical Effect in Living Radical Polymerization–Borderline Cases and Side-Reactions," *CHIMIA International Journal for Chemistry,* vol. 55, pp. 109-113, 2001.

[61] A. Van Herk and R. Gilbert, "Emulsion polymerisation," *Chemistry and Technology of Emulsion Polymerisation, Second Edition,* pp. 43-73, 2013.

[62] S. C. Thickett and R. G. Gilbert, "Emulsion polymerization: state of the art in kinetics and mechanisms," *Polymer,* vol. 48, pp. 6965-6991, 2007.

[63] W. V. Smith and R. H. Ewart, "Kinetics of emulsion polymerization," *The journal of chemical physics,* vol. 16, pp. 592-599, 1948.

[64] A. Chaiyasat, "Role of Emulsifier in Emulsion polymerization," *BUU Sci. J.,* vol. 18, pp. 240-248, 2013.

[65] A. Goodall, M. Wilkinson, and J. Hearn, "Mechanism of emulsion polymerization of styrene in soap-free systems," *Journal of polymer science: Polymer chemistry edition,* vol. 15, pp. 2193-2218, 1977.

[66] J. W. Vanderhoff, "Mechanism of emulsion polymerization," in *Journal of Polymer Science: Polymer Symposia*, 1985, pp. 161-198.

[67] C. Chern, "Emulsion polymerization mechanisms and kinetics," *Progress in polymer science,* vol. 31, pp. 443-486, 2006.

## List of Bibliography (continued)

[68] F. Hansen and J. Ugelstad, "Particle nucleation in emulsion polymerization. I. A theory for homogeneous nucleation," *Journal of Polymer Science: Polymer Chemistry Edition,* vol. 16, pp. 1953-1979, 1978.

[69] R. G. Gilbert, *Emulsion polymerization: a mechanistic approach*: Academic Pr, 1995.

[70] W. D. Harkins, "A general theory of the mechanism of emulsion polymerization1," *Journal of the American Chemical Society,* vol. 69, pp. 1428-1444, 1947.

[71] R. M. Fitch and C. Tsai, "Particle formation in polymer colloids, III: Prediction of the number of particles by a homogeneous nucleation theory," in *Polymer Colloids*, ed: Springer, 1971, pp. 73-102.

[72] C.-S. Chern, *Principles and applications of emulsion polymerization*: John Wiley & Sons, 2008.

[73] Y. Wi, K. Lee, B. H. Lee, and S. Choe, "Soap-free emulsion polymerization of styrene using poly (methacrylic acid) macro-RAFT agent," *Polymer,* vol. 49, pp. 5626-5635, 2008.

[74] M. Manguian, M. Save, and B. Charleux, "Batch Emulsion Polymerization of Styrene Stabilized by a Hydrophilic Macro-RAFT Agent," *Macromolecular rapid communications,* vol. 27, pp. 399-404, 2006.

[75] J. Rieger, F. Stoffelbach, C. Bui, D. Alaimo, C. Jérôme, and B. Charleux, "Amphiphilic poly (ethylene oxide) macromolecular RAFT agent as a stabilizer and control agent in ab initio batch emulsion polymerization," *Macromolecules,* vol. 41, pp. 4065-4068, 2008.

## List of Bibliography (continued)

[76] B. Charleux and J. Nicolas, "Water-soluble SG1-based alkoxyamines: A breakthrough in controlled/living free-radical polymerization in aqueous dispersed media," *Polymer,* vol. 48, pp. 5813-5833, 2007.

[77] C. Dire, S. Magnet, L. Couvreur, and B. Charleux, "Nitroxide-mediated controlled/living free-radical surfactant-free emulsion polymerization of methyl methacrylate using a poly (methacrylic acid)-based macroalkoxyamine initiator," *Macromolecules,* vol. 42, pp. 95-103, 2008.

[78] S. C. Thickett, M. Gaborieau, and R. G. Gilbert, "Extended mechanistic description of particle growth in electrosterically stabilized emulsion polymerization systems," *Macromolecules,* vol. 40, pp. 4710-4720, 2007.

[79] S. C. Thickett, B. Morrison, and R. G. Gilbert, "Particle Size Distributions in Electrosterically Stabilized Emulsion Polymerization Systems: Testing the "Mid-Chain-Radical" Hypothesis," *Macromolecules,* vol. 41, pp. 3521-3529, 2008.

[80] Y. Kitayama, A. Chaiyasat, and M. Okubo, "Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization of Styrene," in *Macromolecular symposia*, 2010, pp. 25-32.

[81] H. Moribe, Y. Kitayama, T. Suzuki, and M. Okubo, "Effect of stirring rate on particle formation in emulsifier-free, organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene," *Polymer journal,* vol. 44, pp. 205-210, 2012.

[82] D. E. Ganeva, E. Sprong, H. De Bruyn, G. G. Warr, C. H. Such, and B. S. Hawkett, "Particle formation in ab initio RAFT mediated emulsion polymerization systems," *Macromolecules,* vol. 40, pp. 6181-6189, 2007.

## List of Bibliography (continued)

[83] N. M. Ranjha, "Swelling behaviour of pH-sensitive crosslinked poly (vinyl acetate co-acrylic acid) hydrogels for site specific drug delivery," *Pakistan journal of pharmaceutical sciences,* vol. 12, pp. 33-41, 1999.

[84] J. Zhang, "Synthesis and characterization of pH-and temperaturesensitive poly (methacylic acid)/poly (N-isopropylacrylamide) interpenetrating polymeric networks," *Macromolecules,* vol. 33, pp. 1102-1107, 2000.

[85] G. Wang and D. Yan, "Preparation of amphiphilic PS-b-PMAA diblock copolymer by means of atom transfer radical polymerization," *Journal of applied polymer science,* vol. 82, pp. 2381-2386, 2001.

# APPENDIX

# ABSTRACT BOOK

## INTERNATIONAL POLYMER CONFERENCE OF THAILAND (PCT-5)

June 18th - 19th, 2015
At Pathumwan Princess Hotel, Bangkok, Thailand
*Annual Meeting for Polymer Science and Technology for Academic Research and Industrial Development*

SESSIONS
- [illegible] and Environmentally Friendly Polymers
- Advances in Polymer Characterization
- Polymer Composites and Nanocomposites
- Advances in Polymer Processing
- Smart and Intelligent Polymers
- Natural and Synthetic Rubbers

Organized by Polymer Society of Thailand (PST)

**SMARTP-06**

# Preparation of polystyrene particles by emulsifier-free emulsion reversible chain transfer catalyzed polymerization (emulsion RTCP) with germanium iodide as catalyst

**Sawitri Sue-eng**[1], Siriwan Thaochattturat[1], Masayoshi Okubo[1, 2], Preeyaporn Chaiyasat[1], Amorn Chaiyasat[a,*]

[1] Department of Chemistry, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Klong6, Thanyaburi, Pathumthani 12110, Thailand
[2] Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan

## Abstract

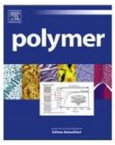
Polymer particles prepared by emulsion polymerization were widely used as films in a variety of industrial applications, for example, paints, paper coatings, and adhesives[1, 2]. Conventional radical polymerization is often used for this technique. However, it lacks of control molecular weight, molecular weight distribution (MWD), the end functionalities and molecular architectures. Controlled/living radical polymerization (CLRP) techniques are then developed to overcome those drawbacks[3, 4]. In this work, one of the most recent CLRP technique, reversible chain transfer catalyzed polymerization (RTCP)[5], was implemented to prepare poly(methacrylic acid)-*b*-polystyrene (PMAA-*b*-PS) particles by emulsifier-free emulsion RTCP with a macro chain transfer agent, potassium persulfate as an initiator and germanium iodide as a catalyst at 60°C in an alkaline condition. PMAA-iodide (PMAA-I) was used as the macro chain transfer agent, which was firstly prepared by solution iodine transfer polymerization (solution ITP) using iodoform as a chain transfer agent and 4,4'-Azobis(4-methoxy-2,4-dimethyvaleronitrile( V-70) as an initiator in dioxane at 60°C . The obtained PMAA-I had a number-average molecular weight ($M_n$) of 1640 g/mol, which indicates an average number of MAA units to be 16, and MWD ($M_w/M_n$) of 2.22. The obtained PMAA-*b*-PS particles had a narrow particle size distribution (weight- and number-average diameters of 244 and 233 nm, respectively). $M_n$ was 52,910 g/mol closed to that of the theoretical value ($M_{n,th}$ ~ 49,020 g/mol), which indicates that the RTCP proceeded with a good livingness.

Polymer 110 (2017) 124–130

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



# Preparation of stable poly(methacrylic acid)-*b*-polystyrene emulsion by emulsifier-free emulsion iodine transfer polymerization (emulsion ITP) with self-assembly nucleation

S. Sue-eng [a], T. Boonchuwong [a], P. Chaiyasat [a, b], M. Okubo [a, c, d, *], A. Chaiyasat [a, b, **]

[a] *Department of Chemistry, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Klong 6, Thanyaburi, Pathumthani 12110, Thailand*

[b] *Advanced Materials Design and Development (AMDD) Research Unit, Institute of Research and Development, Rajamangala University of Technology Thanyaburi, Klong 6, Thanyaburi, Pathumthani 12110, Thailand*

[c] *Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan*

[d] *Institute of Advanced Materials, Nanjing Tech University, 5 Xin Mofan Rood, Nanjing 210009, China*

## ARTICLE INFO

*Article history:*
Received 31 August 2016
Received in revised form
25 December 2016
Accepted 27 December 2016
Available online 28 December 2016

*Keywords:*
Iodine transfer polymerization
Controlled/living radical emulsion polymerization
Emulsion ITP

## ABSTRACT

Emulsifier-free emulsion iodine transfer polymerization (emulsion ITP) of styrene with self-assembly nucleation was successfully carried out with some living features for the first time as follows. Firstly, poly(methacrylic acid) (PMAA; degree of polymerization, 37)-iodide ($PMAA_{37}$-I) as a macro chain transfer agent was synthesized by solution reversible chain transfer catalyzed polymerization (solution RTCP) with 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) as an initiator, iodoform as a chain transfer agent and germanium iodide as a catalyst in dioxane at 40 °C. A dioxane solution of PMAA37-I and styrene were added stepwisely under stirring into an aqueous solution (pH~9), and then emulsion ITP was initiated by adding 4,4′-azobis(4-cyanopentanoic acid) at 60 °C with stirring at 500 rpm. Stable polystyrene emulsion was obtained without coagulation. At 100% conversion, the number-average diameter was 223 nm. Number-average molecular weight ($M_n$) increased linearly with conversion, which were well closed to theoretical $M_n$ and molecular weight distribution at 100% conversion was comparatively narrow ($M_w/M_n$~2.1).

## 1. Introduction

Controlled/living radical polymerization (CLRP) [1–3] has been applied for the synthesis of vinyl polymers having narrow molecular weight distribution (MWD) and design of macromolecular architecture such as block and graft copolymers [2,4]. Several techniques of CLRP have been studied such as nitroxide-mediated polymerization (NMP) [5], atom transfer radical polymerization (ATRP) [6,7], reversible addition fragmentation chain transfer (RAFT) [8] and organotellurium-mediated living radical polymerization (TERP) [9].

Iodine transfer polymerization (ITP) is one of the most popular CLRP techniques (Scheme 1) [10–13] because it is the most ancient CLRP techniques and it has advantages such as low cost reagent, environmentally friendliness, simplicity and non-use of transition metal compounds. In this technique, iodine compounds such as cyanopropyl iodide and iodoform ($CHI_3$) were used for the control of MWD. CLRPs have been firstly developed in homogeneous systems such as bulk and solution polymerizations [2,4]. Thereafter, they were successfully applied to aqueous dispersed systems such as dispersion [14], suspension [15], miniemulsion [16–18], emulsion [19,20] and seeded emulsion polymerizations [21].

Emulsion polymerization is widely applied for industrial polymer production, because of a nontoxic environmental friendly medium, a high polymerization rate and a low shear rate at a high solid content [22,23]. Therefore, CLRP in an emulsion polymerization system (emulsion CLRP) has been studying actively [24–26]. In the system, the locus of polymerization is the polymerizing particle swollen with monomers dispersing in an aqueous medium except for an initial stage, initiator radicals are generated in the aqueous medium, and

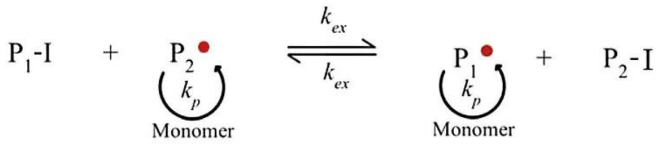
---

* Corresponding author. Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan.

** Corresponding author. Department of Chemistry, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Klong 6, Thanyaburi, Pathumthani 12110, Thailand.

*E-mail addresses:* okubo@kobe-u.ac.jp (M. Okubo), a_chaiyasat@mail.rmutt.ac.th (A. Chaiyasat).

http://dx.doi.org/10.1016/j.polymer.2016.12.067



**Scheme 1.** Iodine transfer polymerization (ITP).

monomer droplets only work as reservoir to supply monomer to the polymerizing particles via the aqueous medium. Therefore, it is difficult for hydrophobic control agents, which are pre-soluble in monomer phase, to diffuse via water into polymerizing particle and coexist with propagating radicals therein. Hawkett and coworkers [27] proposed a clever idea in RAFT emulsion polymerization of n-butyl acrylate (BA) or styrene with water-soluble polyacrylic acid (PAA) oligomer RAFT reagent, which was named self-assembly nucleation. The self-assembly of block copolymers resulted from various kinds of macro chain transfer agents is then used in heterogeneous systems [28] such as in dispersion polymerization [29–31] where the main particles were formed by homogeneous nucleation. In RAFT emulsion polymerization, a water-soluble PAA oligomer radical, which is formed by the reaction of the water-soluble PAA oligomer RAFT reagents with initiator radical [27], adds to hydrophobic monomers dissolved in the aqueous medium to form amphiphilic block oligomer. When the hydrophobic block chain reaches to a critical chain length, at which the hydrophobic block chain precipitates in water, they form micelles by self-assembly. The micelles then are swollen with monomer and the polymerization takes place therein by the entering of initiator radicals from an aqueous medium like a general emulsion polymerization with emulsifier. Thereafter, the other groups successfully applied it in NMP [32–34] and RAFT [24,27,35–38] systems. In our previous works, the self-assembly technique has also been applied in emulsion TERP [39] of BA or styrene [19,20,40,41] using poly(methacrylic acid) (PMAA; degree of polymerization: 30)-methyltellanyl (TeMe) ($PMAA_{30}$-TeMe) as a control agent, in which PMAA block was used in place of PAA block to avoid back biting reaction [42,43].

In this article, emulsion ITP of styrene will be carried out for the first time using PMAA-I, which was prepared by reversible chain transfer catalyzed polymerization (RTCP) [44], as a macro chain transfer agent.

## 2. Experimental

### 2.1. Materials

Styrene (Aldrich; purity, 99%) and methacrylic acid (MAA) (Aldrich; purity, 99%) were purified by pass through the column packed with basic aluminum oxide. 2,2′-Azobis (4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako Pure Chemicals), iodoform ($CHI_3$) (Aldrich; purity, 99%), germanium (IV) iodide ($GeI_4$) (Aldrich; purity, 99%) and dioxane (Lab scan; purity 98%) were used as received. 4,4′-Azobis(4-cyanopentanoic acid) (V-501) (Wako Pure Chemicals), trimethylsilyldiazomethane (TMSD) (Acros; purity, 99%), acetic acid (Lab scan; purity, 98%), potassium hydroxide (KOH) (Univar; purity, 97%) and dimethylformamide (DMF) (Lab scan; purity, 98%) were used without purification. Deionized water with a specific resistance of 18 MΩ cm was distilled before use.

### 2.2. Synthesis of PMAA-I macro chain transfer agent

PMAA-I as macro chain transfer agent was synthesized by solution RTCP [45] as follows. MAA (6.5 g, 75.5 mmol), $CHI_3$ (2.0 g, 5.0 mmol), $GeI_4$ ($2.2 \times 10^{-2}$ g, $3.8 \times 10^{-2}$ mmol) and V-70 (1.2 g, 3.7 mmol) as an initiator were dissolved in dioxane (35.0 g) and added into a round-bottom Schlenk flask. The flask was then closed off with a silicone rubber septum and degassed using several $N_2$/vacuum cycles and finally in $N_2$. It was placed into an oil bath at 40 °C for 24 h. The obtained PMAA-I macro chain transfer agent solution was directly used in the emulsion ITP without purification.

### 2.3. Synthesis of emulsion ITP of styrene

Emulsion ITP of styrene using the $PMAA_{37}$-I macro chain transfer agent was carried out at 60 °C at a stirring rate of 500 rpm with a magnetic stirrer as follows. Styrene (10.4 g, 100.0 mmol) and V-501 (70.0 mg, $25.0 \times 10^{-2}$ mmol) as initiator were added into an aqueous solution (90.0 g) containing $PMAA_{37}$-I ($25.0 \times 10^{\ 2}$ mmol, 6.5 g of dioxane solution containing $PMAA_{37}$-I 14.6 wt%), of which pH was uncontrolled (pH~4) or controlled (pH~9) by KOH solution. Samples were withdrawn with a syringe and the polymerization was stopped with a few drops of hydroquinone aqueous solution (1.0 wt%).

### 2.4. Characterizations

Monomer conversion was measured by gravimetry. Emulsion samples (~2.0 g) taken from the reactor were transferred directly into aluminum cup and weighted. Several drops of hydroquinone solution (1 wt%) were added therein before the free liquid was evaporated in an oven at 70 °C. The sample was dried until a constant weight of the dried polymer was obtained. Monomer conversion was obtained by comparing the weight of dried polymer with that of the original monomer. Weight- and number-average molecular weights ($M_w$ and $M_n$, respectively) and MWD were measured by gel permeation chromatography (GPC) (Waters 2414, Waters, USA) with two poly(styrene/divinylbenzene) gel columns (Phenogel $5 \times 10^2$ and $3 \times 10^5$ Å (pores), 7.8 mm (i.d) × 30 cm (length), Phenomenex, USA) connected in series and using THF as eluent. The flow rate of eluent was maintained at 1.0 mL/min with column temperature of 40 °C and elution was monitored with refractive index detector. The columns were calibrated with six standard PS samples ($2.5 \times 10^3$–$6.0 \times 10^5$, $M_w/M_n = 1.05$–$1.15$). Before measurement, PMAA-I and PMAA-*b*-PS were modified by methylation of the carboxyl group using TMSD as follows. PMAA-I and PMAA-*b*-PS samples were dried at room temperature before dissolving in DMF. Then, several droplets of TMSD was added into the polymer solutions, in which the reaction was allowed to continue overnight (PMAA form is changed to poly(methyl methacrylate) (PMMA) form). After excess TMSD was destroyed by acetic acid, the methylated polymers were precipitated by dropwise addition of the 1 wt% of DMF solution into 15 mL of methanol, and filtrated. The dried polymers were separately dissolved in THF (1 wt%) before GPC measurement. Theoretical number-average molecular weight ($M_{n,th}$) was calculated by the following equation:

$$M_{n,th} = MW_{PMAA_{37}-I} + \left(\frac{[M]_0 \cdot MW_M \cdot \alpha}{[PMAA_{37} - I]_0 \cdot 100}\right) \tag{1}$$

Where $\alpha$ is the monomer conversion (%), $MW_M$ and $MW_{PMAA_{37}-I}$ are the molecular weights of styrene and $PMAA_{37}$-I, respectively, and $[M]_0$ and $[PMAA_{37}\text{-}I]_0$ are the initial moles of styrene and PMAA-I, respectively. Weight- and number-average diameters ($d_w$ and $d_n$, respectively) were measured by dynamic light scattering (DLS, Delsa Nano C, Beckman Coulter, Germany) at the light scatting angle of 165° at room temperature. The emulsion samples (approximately 10 wt%) withdrawn from the reactor were directly measured with the concentration mode.

## 3. Results and discussion

To implement emulsion ITP with the self-assembly nucleation, PMAA-I was firstly synthesized by solution RTCP using V-70 as an initiator and $GeI_4$ as a catalyst in dioxane at 40 °C. Based on our previous works on emulsion TERP with PMAA-TeMe [19,20,39–41], the obtained PMAA-I was used as water-soluble macro chain transfer agent. The solution RTCP smoothly proceeded and the monomer conversion attained at 100% for 24 h. $M_n$ of the obtained PMAA-I at 100% conversion was about 3800 with $M_w/M_n$ of 1.6 (by GPC), which corresponded to 37 units of MAA ($PMAA_{37}$-I) (Fig. 1). The $PMAA_{37}$-I was used as a macro chain transfer agent in the further emulsion ITP. The residual $CHI_3/GeI_4$ that existed in the $PMAA_{37}$-I macro-CTA dioxane solution do not dissolve in water, whereas the other components such as dioxane and $PMAA_{37}$-I macro-CTA are miscible with water. Then, $CHI_3/GeI_4$ should precipitate out in aqueous media of the emulsion ITP. Even if, they diffuse into the polymerizing particles and participate the polymerization therein, it should be the positive effect for emulsion ITP.

Fig. 2 shows conversion versus time plots of emulsion ITP of styrene using $PMAA_{37}$-I as a macro chain transfer agent and V-501 as an initiator at pH~4 and pH~9 (by KOH) at 60 °C. At the pH~4, the polymerization slowly proceeded and reached 45% conversion for 24 h, which was much slower than that of pH~9 (100% conversion for 24 h). As shown in Fig. 3, $d_n$ values of PS particles were 714 nm, 1182 nm and 1804 nm at 9%, 15% and 24% conversions, respectively, and it further attained above 4 μm at 45% conversion. Both homogeneous nucleation of PS chains without PMAA-block (the larger size) and self-assembly nucleation of $PMAA_{37}$-*b*-PS (smaller size; ~100–200 nm) seemed occurring throughout the polymerization at pH 4 according to previous works [19,20,39–41]. In an early stage of the polymerization, both particle formations were not significantly different. However, particle coagulation would be the main reason to obtain the higher number of larger particle than that of the smaller one although a bimodal of size distributions was only observed at 24% conversion. After 24% conversion, the smaller size particles apparently disappeared because of adsorption onto the bigger size particles. The size of the remained particles (micrometer-size) increased with the conversion based on not only the polymerization but also the coalescence among the unstable smaller particles of block copolymer self-assembly, unstable homogenoueos nucleated particles and unstable larger particles. These indicate that the coagulation of particles began from the initial stage and continued throughout the polymerization. Because pKa of PMAA in an aqueous solution is 5.55–5.65 [46,47], the carboxyl groups of PMAA37-I scarcely ionize at the pH~4. Therefore, under the condition, PMAA chains do not operate effectively to stabilize forming particles as hairy layer at the particle surfaces. Moreover, a part of the unionized PMAA37-I may adsorb at the interface of styrene droplets and cannot act as the macro chain transfer agent, which reduces the efficiency of the formation of $PMAA_{37}$-*b*-PS-I in the aqueous medium in the early stage of the polymerization. In addition, the adsorbed $PMAA_{37}$-I desorbs from the monomer droplet surface due to decrease of surface area of the droplets, which operate as monomer reservoir, with polymerization resulting in the formation of new particles throughout the polymerization with the self assembly of $PMAA_{37}$-*b*-PS-I until monomer droplets disappear in the system even if most of the smaller sizes were not detected with DLS in all conversions except at 24% conversion. In actual, at 24% conversion, the amount of formed particles with both mechanisms may not significantly different where the MWD curve having shoulder at higher molecular weight (homogeneous nucleation) was clearly observed as shown in Fig. 4a. Thereafter, $M_w/M_n$ value attained 3 at 45% conversion although $M_n$ values were apparently closed to $M_{n,th}$ value and linearly increased with the conversion.

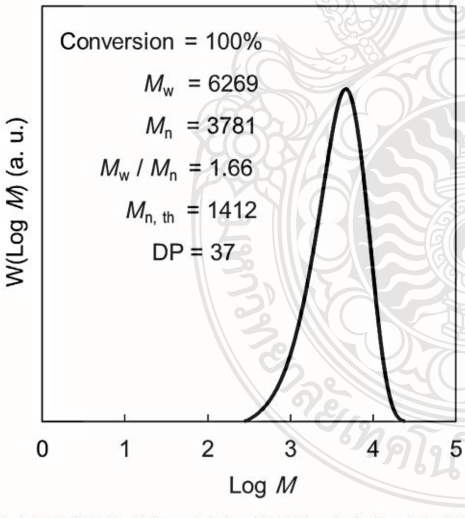


**Fig. 1.** MWD of $PMMA_{37}$-I (after methylation with TMSD) synthesized by solution RTCP of MAA with $CHI_3$ as a control agent, V-70 as an initiator and $GeI_4$ as a catalyst.

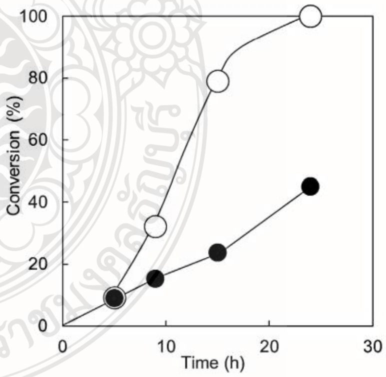


**Fig. 2.** Conversion versus time plots of $PMAA_{37}$-*b*-PS prepared by emulsion ITP at 60 °C at pH~4 (closed circles) and pH~9 (open circles) using styrene/$PMAA_{37}$-I/V-501 (molar ratio) = 400/1/1.

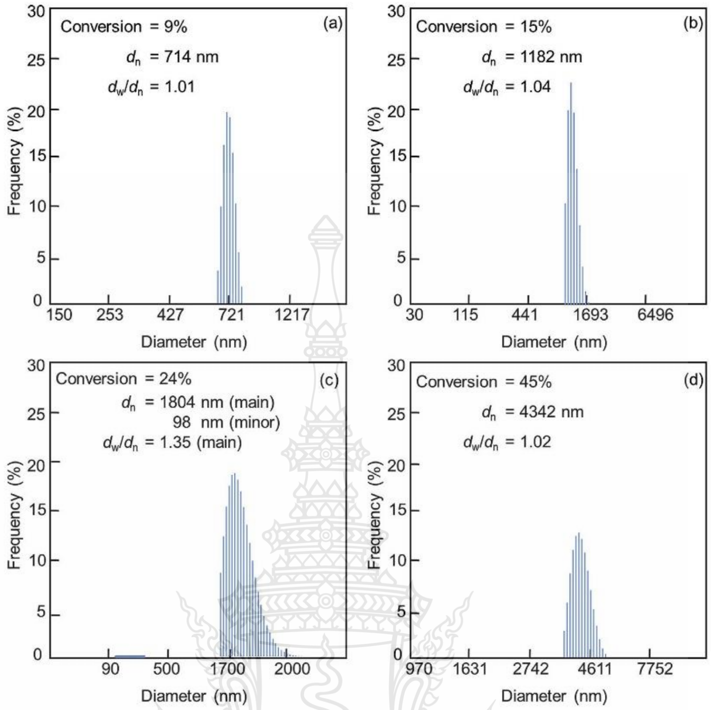


**Fig. 3.** Particle size distributions (number distribution) (measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP at 60 °C at pH~4 using styrene/PMAA$_{37}$-I/V-501(molar ratio) = 400/1/1 at different conversions: (a) 9; (b) 15; (c) 24; (d) 45.

On the other hand, when the emulsion ITP was carried out at pH~9, at which all of carboxyl groups of PMAA37-I ionize, the $d_n$ value was 119 nm at 9% conversion (Fig. 5a) and monomodal particle size distribution was maintained throughout the polymerization (Fig. 5a–d). Even at 100% conversion, it was 223 nm (Fig. 5d). These indicate that the emulsion ITP proceeded without coagulation. Because larger number of ionized carboxyl group in PMAA$_{37}$-I chain are given at pH~9, the formed particles are much

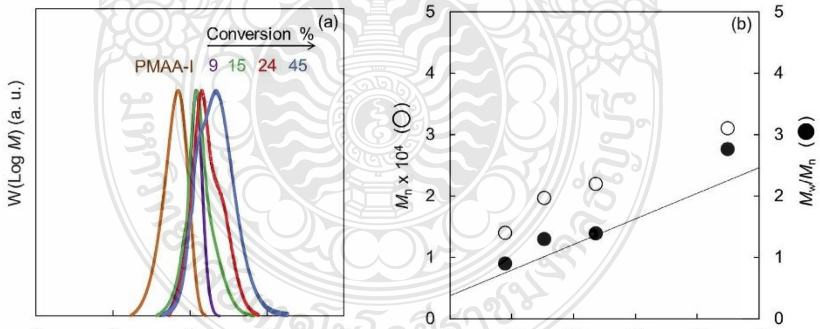


**Fig. 4.** MWDs (a) and $M_n$ (open circles) and $M_w/M_n$ (closed circles) (b) at different conversions of PMMA$_{37}$-*b*-PS (after methylation TMSD) prepared by emulsion ITP at 60 °C at pH~4 using styrene/PMAA$_{37}$-I/V-501 (molar ratio) = 400/1/1. The straight line is $M_{n,th}$.

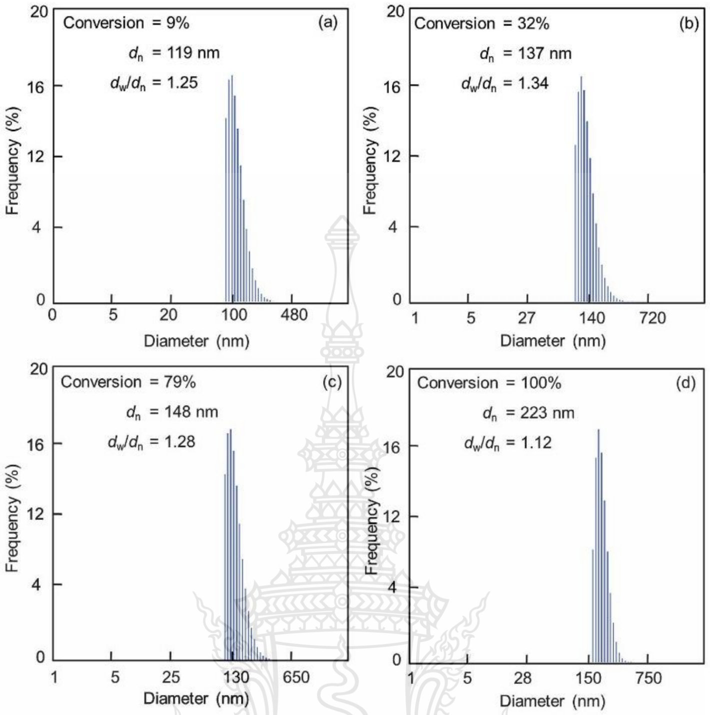
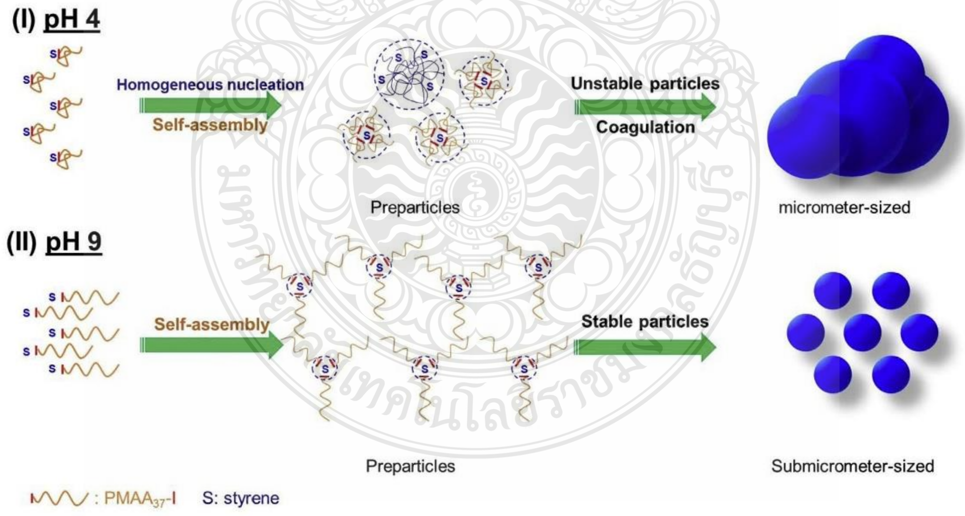


**Fig. 5.** Particle size distributions (number distribution) (measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP at 60 °C at pH~9 using styrene/PMAA$_{37}$-I/V-501 (molar ratio) = 400/1/1 at different conversions (%): (a) 9; (b) 32; (c) 79; (d) 100.



**Scheme 2.** Emulsion ITP with self-assembly nucleation at acidic or alkaline pH.

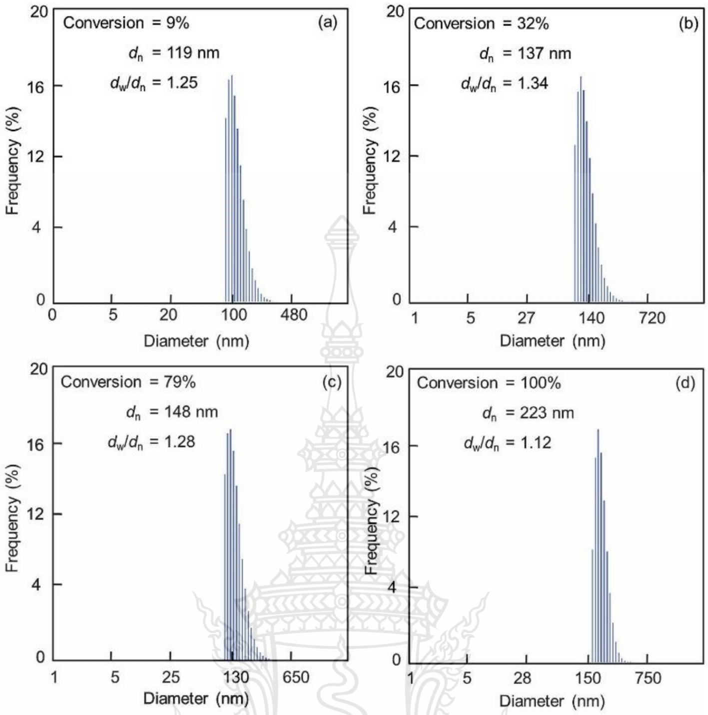
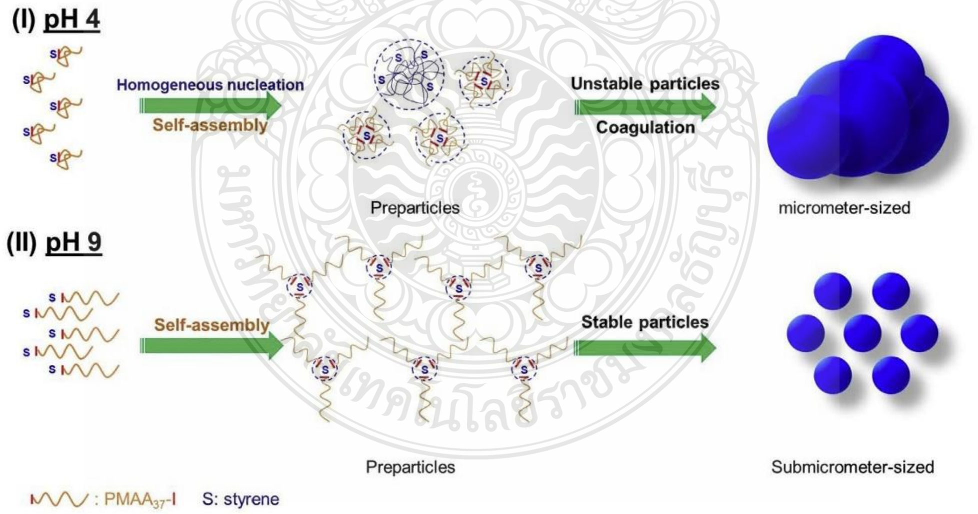


**Fig. 5.** Particle size distributions (number distribution) (measured by DLS) of PMAA-*b*-PS particles prepared by emulsion ITP at 60 °C at pH~9 using styrene/$PMAA_{37}$-I/V-501 (molar ratio) = 400/1/1 at different conversions (%): (a) 9; (b) 32; (c) 79; (d) 100.



**Scheme 2.** Emulsion ITP with self-assembly nucleation at acidic or alkaline pH.

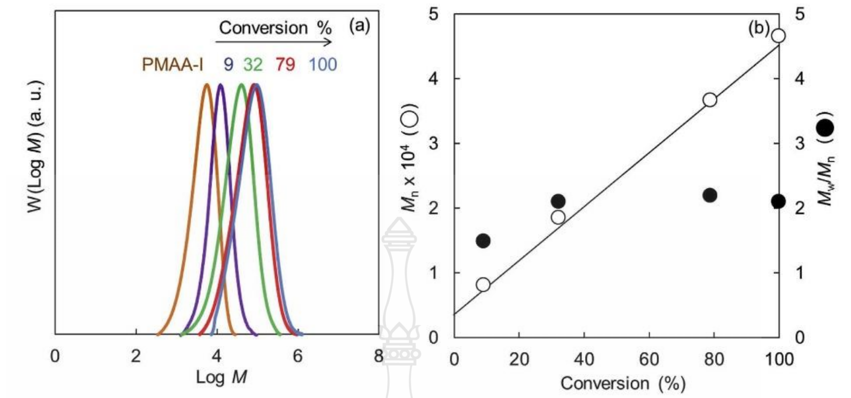


**Fig. 6.** MWDs (a) and $M_n$ (open circles) and $M_w/M_n$ (closed circles) (b) at different conversions of PMMA$_{37}$-*b*-PS (after methylation TMSD) prepared by emulsion ITP at 60 °C at pH~9 using styrene/PMAA$_{37}$-I/V-501 (molar ratio) = 400/1/1. The straight line is $M_{n,th}$.

more stable than at pH~4. The mechanism proposed for emulsion ITP with self-assembly nucleation at both pH is illustrated in Scheme 2.

Fig. 6 shows MWDs, $M_n$ and $M_w/M_n$ at different conversions of the emulsion ITP at pH~9. The MWD, in which any shoulder was not observed at each conversion, shifted to the higher molecular weight maintaining a relatively narrow distribution with increasing conversion. The $M_n$ value increased linearly with conversion and well agreed with the $M_{n,th}$ at each conversion (Fig. 6b). The $M_w/M_n$ values were relatively low (~2.0) throughout the polymerization. Although, the molecular weight of PMMA-*b*-PS (after methylation) measured by GPC using PS standard may not linearly correlate to their absolute molecular weight. However, because the PMMA-*b*-PS prepared in this study has a short PMMA block (degree of polymerization was 37) in comparison with PS block, the obtained $M_n$ would not be significantly different from the absolute one.

By the comparison with PMMA$_{37}$-I (after methylation), MWD of PMAA-*b*-PS shifted to higher molecular weight with keeping a narrow MWD even at 9% conversion, where the weights of original PMAA$_{37}$-I and PS in the system were nearly the same. There was no shoulder at lower molecular weight side in the MWD at 9% conversion, which indicates that most of PMAA$_{37}$-I acted as the macro chain transfer agent in the early stage of the emulsion ITP and added styrene monomers, resulting in PMAA-*b*-PS. That is, the emulsion ITP using PMAA$_{37}$-I macro chain transfer agent proceeded with some living features at the alkaline condition. From these results, it is concluded that the emulsion ITP of styrene using PMAA$_{37}$-I/V-501 was successfully carried out with self-assembly nucleation at the alkaline condition (pH~9).

## 4. Conclusions

Emulsion ITP of styrene was successfully carried out with the self-assembly nucleation for the first time using the PMAA$_{37}$-I macro chain transfer agent and V-501 initiator at 60 °C under alkaline pH. The polymerization proceeded smoothly and completed for one day. The $d_n$ value of the obtained PS particles at 100% conversion was 223 nm. The $M_n$ value increased linearly with the conversion and well agreed with the $M_{n,th}$ at each conversion. The MWDs were comparatively narrow ($M_w/M_n$~2). These results indicate that the emulsion ITP proceeded with some living features.

## Acknowledgements

This work was supported by The RMUTT annual government statement of expenditure in 2014 (NRMS 2557A16502025; given to A.C. and P.C.), and by Grant-in-Aid for Scientific Research (B) (Grant 25288054; given to M.O.) from the Japan Society for the Promotion of Science (JSPS).

## References

[1] P.B. Zetterlund, Y. Kagawa, M. Okubo, Controlled/living radical polymerization in dispersed systems, Chem. Rev. 108 (9) (2008) 3747–3794.
[2] W.A. Braunecker, K. Matyjaszewski, Erratum to: "Controlled/living radical polymerization: features, developments and perspectives", Prog. Polym. Sci. 32 (2007) 93–146. Prog. Polym. Sci. 33(1) (2008) 165.
[3] J. Qiu, B. Charleux, K. Matyjaszewski, Controlled/living radical polymerization in aqueous media: homogeneous and heterogeneous systems, Prog. Polym. Sci. 26 (2001) 2083–2134.
[4] H. Gao, K. Matyjaszewski, Synthesis of functional polymers with controlled architecture by CRP of monomers in the presence of cross-linkers: from stars to gels, Prog. Polym. Sci. 34 (4) (2009) 317–350.
[5] M.K. Georges, R.P.N. Veregin, P.M. Kazmaier, G.K. Hamer, Narrow molecular weight resins by a free-radical polymerization process, Macromolecules 26 (11) (1993) 2987–2988.
[6] J.-S. Wang, K. Matyjaszewski, Controlled/"living" radical polymerization. Atom transfer radical polymerization in the presence of transition-metal complexes, J. Am. Chem. Soc. 117 (20) (1995) 5614–5615.
[7] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris- (triphenylphosphine)ruthenium(II)/methylaluminum Bis(2,6-di-tert-butylphenoxide) initiating system: possibility of living radical polymerization, Macromolecules 28 (5) (1995) 1721–1723.
[8] J. Chiefari, Y.K. Chong, F. Ercole, J. Krstina, J. Jeffery, T.P.T. Le, R.T.A. Mayadunne, G.F. Meijs, C.L. Moad, G. Moad, E. Rizzardo, S.H. Thang, Living free-radical polymerization by reversible addition–fragmentation chain transfer: the RAFT process, Macromolecules 31 (16) (1998) 5559–5562.
[9] S. Yamago, K. Iida, J.-i. Yoshida, Tailored synthesis of structurally defined polymers by organotellurium-mediated living radical polymerization (TERP): synthesis of poly(meth)acrylate derivatives and their di- and triblock copolymers, J. Am. Chem. Soc. 124 (46) (2002) 13666–13667.
[10] M. Tatemoto, M. Tomoda, Y. Ueda, U.S. Patent (1981).
[11] C. Boyer, D. Valade, L. Sauguet, B. Ameduri, B. Boutevin, Iodine transfer polymerization (ITP) of Vinylidene Fluoride (VDF). Influence of the defect of VDF chaining on the control of ITP, Macromolecules 38 (25) (2005) 10353–10362.
[12] K. Matyjaszewski, S. Gaynor, J.-S. Wang, Controlled radical polymerizations: the use of alkyl iodides in degenerative transfer, Macromolecules 28 (6) (1995) 2093–2095.
[13] S.G. Gaynor, J.-S. Wang, K. Matyjaszewski, Controlled radical polymerization by degenerative transfer: effect of the structure of the transfer agent,

Macromolecules 28 (24) (1995) 8051–8056.

[14] T. Kuroda, A. Tanaka, T. Taniyama, H. Minami, A. Goto, T. Fukuda, M. Okubo, Iodine transfer dispersion polymerization (dispersion ITP) with CHI3 and reversible chain transfer catalyzed dispersion polymerization (dispersion RTCP) with GeI4 of styrene in supercritical carbon dioxide, Polymer 53 (6) (2012) 1212–1218.

[15] J.D. Biasutti, T.P. Davis, F.P. Lucien, J.P.A. Heuts, Reversible addition—-fragmentation chain transfer polymerization of methyl methacrylate in suspension, J. Polym. Sci. Part A Polym. Chem. 43 (10) (2005) 2001–2012.

[16] S. Liu, K.D. Hermanson, E.W. Kaler, Reversible addition–fragmentation chain transfer polymerization in microemulsion, Macromolecules 39 (13) (2006) 4345–4350.

[17] K.D. Hermanson, S. Liu, E.W. Kaler, Kinetic modeling of controlled living microemulsion polymerizations that use reversible addition–fragmentation chain transfer, J. Polym. Sci. Part A Polym. Chem. 44 (20) (2006) 6055–6070.

[18] P.B. Zetterlund, M.N. Alam, H. Minami, M. Okubo, Nitroxide-mediated controlled/living free radical copolymerization of styrene and divinylbenzene in aqueous miniemulsion, macromol, Rapid Commun. 26 (12) (2005) 955–960.

[19] Y. Kitayama, H. Moribe, H. Minami, M. Okubo, Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of styrene: initial stage of polymerization, Polymer 52 (13) (2011) 2729–2734.

[20] Y. Kitayama, A. Chaiyasat, H. Minami, M. Okubo, Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of styrene: polymerization loci, Macromolecules 43 (18) (2010) 7465–7471.

[21] M. Okubo, H. Minami, J. Zhou, Preparation of block copolymer by atom transfer radical seeded emulsion polymerization, Colloid. Polym. Sci. 282 (7) (2003) 747–752.

[22] M.F. Cunningham, Living/controlled radical polymerizations in dispersed phase systems, Prog. Polym. Sci. 27 (6) (2002) 1039–1067.

[23] S.C. Thickett, R.G. Gilbert, Emulsion polymerization: state of the art in kinetics and mechanisms, Polymer 48 (24) (2007) 6965–6991.

[24] K. Yan, X. Gao, Y. Luo, Well-defined high molecular weight polystyrene with high rates and high livingness synthesized via two-stage RAFT emulsion polymerization, Macromol. Rapid Commun. 36 (13) (2015) 1277–1282.

[25] J. Nicolas, Y. Guillaneuf, C. Lefay, D. Bertin, D. Gigmes, B. Charleux, Nitroxide-mediated polymerization, Prog. Polym. Sci. 38 (1) (2013) 63–235.

[26] M.J. Monteiro, M.F. Cunningham, Polymer nanoparticles via living radical polymerization in aqueous dispersions: design and applications, Macromolecules 45 (12) (2012) 4939–4957.

[27] C.J. Ferguson, R.J. Hughes, B.T.T. Pham, B.S. Hawkett, R.G. Gilbert, A.K. Serelis, C.H. Such, Effective ab initio emulsion polymerization under RAFT control, Macromolecules 35 (25) (2002) 9243–9245.

[28] S.L. Canning, G.N. Smith, S.P. Armes, A Critical appraisal of RAFT-mediated polymerization-induced self-assembly, Macromolecules 49 (6) (2016) 1985–2001.

[29] L. Qiu, C.-R. Xu, F. Zhong, C.-Y. Hong, C.-Y. Pan, Fabrication of functional nano-objects through RAFT dispersion polymerization and Influences of morphology on drug delivery, ACS Appl. Mater. Interfaces 8 (28) (2016) 18347–18359.

[30] C. Gao, J. Wu, H. Zhou, Y. Qu, B. Li, W. Zhang, Self-assembled blends of AB/BAB block copolymers prepared through dispersion RAFT polymerization, Macromolecules 49 (12) (2016) 4490–4500.

[31] P. Chambon, A. Blanazs, G. Battaglia, S.P. Armes, Facile synthesis of methacrylic ABC triblock copolymer vesicles by RAFT aqueous dispersion polymerization, Macromolecules 45 (12) (2012) 5081–5090.

[32] K. Shen, D. Qi, Y. Li, X. Zhao, Y. Li, Amphiphilic tertiary amine N-oxides: a mediated radical emulsion polymerization with non-formation of alkoxyamine dormant chains, Chem. Commun. 51 (50) (2015) 10166–10169.

[33] E. Groison, S. Brusseau, F. D'Agosto, S. Magnet, R. Inoubli, L. Couvreur, B. Charleux, Well-Defined amphiphilic block copolymer nanoobjects via nitroxide-mediated emulsion polymerization, ACS Macro Lett. 1 (1) (2012) 47–51.

[34] M.E. Thomson, A.-M. Manley, J.S. Ness, S.C. Schmidt, M.F. Cunningham, Nitroxide-mediated surfactant-free emulsion polymerization of n-butyl methacrylate with a small amount of styrene, Macromolecules 43 (19) (2010) 7958–7963.

[35] J. Rieger, G. Osterwinter, C. Bui, F. Stoffelbach, B. Charleux, Surfactant-free controlled/living radical emulsion (Co)polymerization of n-butyl acrylate and methyl methacrylate via RAFT using amphiphilic poly(ethylene oxide)-based trithiocarbonate chain transfer agents, Macromolecules 42 (15) (2009) 5518–5525.

[36] M.G. Isabelle Chaduc, Rodolphe Antoine, Bernadette Charleux, Franck D'Agosto, Muriel Lansalot, Batch emulsion polymerization mediated by poly(methacrylic acid) MacroRAFT agents: one-pot synthesis of self-stabilized particles, Macromolecules 45 (2012) 5881–5893.

[37] C.J. Ferguson, R.J. Hughes, B.T.T. Pham, B.S. Hawkett, R.G. Gilbert, A.K. Serelis, C.H. Such, Effective ab Initio emulsion polymerization under RAFT control, Macromolecules 35 (2002) 9243–9245.

[38] I. Uzulina, S. Kanagasabapathy, J. Claverie, Reversible addition fragmentation transfer (RAFT) polymerization in emulsion, Macromol. Symp. 150 (2000) 33–38.

[39] M. Okubo, Y. Sugihara, Y. Kitayama, Y. Kagawa, H. Minami, Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of butyl acrylate, Macromolecules 42 (6) (2009) 1979–1984.

[40] H. Moribe, Y. Kitayama, T. Suzuki, M. Okubo, Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of styrene: effect of stirring rate, Macromolecules 44 (2) (2011) 263–268.

[41] Y. Kitayama, A. Chaiyasat, M. Okubo, Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of styrene, Macromol. Symp. 288 (1) (2010) 25–32.

[42] S.C. Thickett, M. Gaborieau, R.G. Gilbert, Extended mechanistic description of particle growth in electrosterically stabilized emulsion polymerization systems, Macromolecules 40 (13) (2007) 4710–4720.

[43] S.C. Thickett, B. Morrison, R.G. Gilbert, Particle size distributions in electrosterically stabilized emulsion polymerization systems: testing the "Mid-Chain-Radical" hypothesis, Macromolecules 41 (10) (2008) 3521–3529.

[44] A. Goto, Y. Tsujii, T. Fukuda, Reversible chain transfer catalyzed polymerization (RTCP): a new class of living radical polymerization, Polymer 49 (24) (2008) 5177–5185.

[45] S. Thaochatturata, M. Okubo, A. Chaiyasat, P. Chaiyasat, Synthesis of poly(-methacrylic acid)-b-polystyrene particles by emulsion reversible chain transfer catalyzed polymerization (emulsion RTCP) using hydroquinone as catalyst, in: 12th Eco-Energy and Materials Science and Engineering Symposium, Krabi, Thailand, 2015, pp. 163–166.

[46] N.M. Ranjha, Swelling behaviour of pH-sensitive crosslinked poly(vinyl acetate co-acrylic acid) hydrogels for site specific drug delivery, Pak. J. Pharm. Sci. 12 (1999) 33–41.

[47] J. Zhang, N.A. Peppas, Synthesis and characterization of pH- and temperature-sensitive poly(methacrylic acid)/poly(N-isopropylacrylamide) interpenetrating polymeric networks, Macromolecules 33 (1) (2000) 102–107.

# Biography

| | |
|---|---|
| **Name-Surname** | Miss. Sawitree Sue-eng |
| **Date of Birth** | November 17, 1990 |
| **Address** | No. 55 Potan, Ongkharak, Nakhon Nayok, 26120, thailand |
| **Education** | Master of Innovative Chemistry |
| **Experiences Work** | Quality Assurance at Nestle (Thailand) Co.,Ltd. |
| **Telephone Number** | +66899680289 |
| **Email Address** | Sawitree6685@gmail.com |