

Termal Olarak Geniřletilebilir Mikrokürelere Hazırlanması Ve Karakterizasyonu

Abu Jafar SIDDIQUI

**YÜKSEK LİSANS TEZİ**

Kimya Mühendisliđi Anabilim Dalı

Mart 2022



Preparation and Characterization of Thermally Expandable Microspheres

Abu Jafar SIDDIQUI

**MASTER OF SCIENCE THESIS**

Department of Chemical Engineering

March 2022

# Preparation and Characterization of Thermally Expandable Microspheres

A thesis submitted to the Eskişehir Osmangazi University  
Graduate School of Natural and Applied Sciences in partial  
fulfillment of the requirements for the degree of Master of Science  
in Discipline of Process and Reactor Design of the Department of Chemical Engineering

by

Abu Jafar SIDDIQUI

Supervisor: Prof. Dr. Macid NURBAŞ

March 2022

## **ETHICAL STATEMENT**

I hereby declare that this thesis study titled “Preparation and Characterization of Thermally Expandable Microspheres” has been prepared in accordance with the thesis writing rules of Eskişehir Osmangazi University Graduate School of Natural and Applied Sciences under academic consultancy of my supervisor Prof. Dr. Macid NURBAŞ. I hereby declare that the work presented in this thesis is original. I also declare that, I have respected scientific ethical principles and rules in all stages of my thesis study, all information and data presented in this thesis have been obtained within the scope of scientific and academic ethical principles and rules, all materials used in this thesis which are not original to this work have been fully cited and referenced, and all knowledge, documents and results have been presented in accordance with scientific ethical principles and rules.

07/03/2022

Abu Jafar SIDDIQUI

## ÖZET

Termal olarak genleşebilen çekirdek-kabuk polimerik mikroküreler süspansiyon polimerizasyonu ile hazırlanmıştır. Çekirdek kısmında şişirici ajan olan farklı uçucu hidrokarbonlar ve kabuk kısmında ise çeşitli monomerlerden sentezlenen polimerik yapı kullanılmıştır. Şişirici ajanı buharlaştıracak kadar ısı uygulandığında, iç basınçta bir değişiklik meydana gelir, bu da mikrokürelerin hacminde çarpıcı bir genişlemeye sebep olur. Bu benzersiz özellik, mikroküreleri hafif dolgu maddesi olarak veya genleşebilir maddeler olarak uygulanabilir hale getirir. Bu çalışmada, kaynama noktaları birbirinden farklı olan şişirici ajanlar kullanılarak poli (akrilonitril-ko-metil metakrilat) çekirdek-kabuk mikroküreler sentezlenmiştir. Mikrokürelerin morfolojisi üzerindeki başlatıcının etkisini incelemek için iki farklı başlatıcı AIBN ve LPO kullanılmıştır. Mikrokapsüllerin morfolojisini iyileştirmek için de NaCl elektroliti kullanılmıştır. İstenmeyen ikincil parçacıkların oluşumunu önlemek için NaNO<sub>2</sub> gibi inhibitörün etkisi, başlatıcı olarak AIBN kullanıldığında incelenmiştir. Çekirdekte kullanılan malzemelerin mikrokürelerin genişleme performansını üzerine etkisini incelemek için tek bileşenli izopentan, n-pentan ve n-heksan gibi uçucu hidrokarbonlar ve ikili bileşenli n-heksan ve heptan, izopentan ve n-pentan, n-heksan ve n-oktan gibi hidrokarbonlar (1:1 oranında) kullanılmıştır. Çekirdek malzemesi olarak birebir oranında n-heksan ve n-oktan karışımı kullanıldığında, %40 AN ve %60 MMA monomerlerin polimerizasyonu ile %29.7 şişirici ajan içeriğine sahip kapsüllenmiş mikroküreler elde edilmiştir. Çekirdekte kullanılan tek bileşeli organik malzemesi yerine ikili organik madde kombinasyonu ile mikrokürelerin genleşme performansında ve kapsüllenmiş uçucu organik madde içeriğinde önemli ölçüde iyileştirme sağlanmıştır. Mikrokürelerin morfolojisini, çekirdek-kabuk yapısını, kapsüllenmiş içeriğini, kimyasal yapısını ve termal özelliklerini karakterize etmek için SEM, TEM, TGA, FTIR ve DTA analizi cihazları kullanılmıştır.

**Anahtar Kelimeler :** Mikroküre, süspansiyon polimerizasyonu, çekirdek-kabuk yapısı, şişirici ajanı

## SUMMARY

Thermally expandable microspheres were prepared by the suspension polymerization process in which different volatile hydrocarbons were encapsulated by polymer shells having various monomer compositions. When heat is applied enough to vaporize the blowing agent, a change in internal pressure occurs, resulting in a dramatic expansion of the volume of the microspheres. This unique property makes the microspheres applicable as lightweight fillers and foaming agents.

In this thesis, microspheres with a poly (acrylonitrile-*co*- methyl methacrylate) shell have been synthesized with different blowing agents having different boiling points. To further investigate the influence of the initiator on the morphology of the microspheres, two different initiators AIBN and LPO were used. NaCl electrolyte was used to improve the morphology of the microcapsules. The effect of inhibitors like NaNO<sub>2</sub> was examined when AIBN was used as an initiator to prevent the formation of secondary particles. Volatile hydrocarbons like isopentane, n-pentane, and n-hexane as single-core material and a mixture of hydrocarbons like n-hexane and heptane, isopentane and n-pentane, n-hexane and n-octane (ratio 1:1) were used to compare the expansion performance. Microspheres with 29.7% encapsulated content of blowing agent was found with the monomers composition of 40 per cent AN/60 percent MMA when a mixture of n-hexane and n-octane (ratio 1:1) was used as the core material. The expansion performance and encapsulated content were improved significantly with mixed core material compared to single core material. SEM, TEM, TGA, FTIR, and DTA analysis were employed to characterize the morphology, core-shell structure, encapsulated content, chemical structure and thermal properties of the microspheres.

**Keywords:** Microsphere, suspension polymerization, core-shell structure, blowing agent

## LIST OF CONTENTS

	<u>Page</u>
<b>ÖZET</b> .....	v
<b>SUMMARY</b> .....	vi
<b>LIST OF CONTENTS</b> .....	vii
<b>LIST OF FIGURES</b> .....	ix
<b>LIST OF TABLES</b> .....	xi
<b>LIST OF ABBREVIATIONS AND SYMBOLS</b> .....	xii
<b>1. INTRODUCTION AND OBJECTIVE</b> .....	1
<b>2. LITERATURE REVIEW</b> .....	5
2.1. Microencapsulation Technology .....	5
2.2. Microcapsule Structure and Encapsulant Materials .....	5
2.3. Theoretical considerations of the release characteristics of encapsulated material ..	7
2.4. Methods for Microcapsule preparation .....	8
2.4.1. Polymerization Processes .....	8
2.4.1.1. <u>Interfacial polymerization</u> .....	9
2.4.2. Physicochemical Methods .....	9
2.4.2.1. <u>Emulsification/solvent evaporation</u> .....	9
2.4.2.2. <u>Coacervation/Phase separation</u> .....	10
2.5. Free Radical Polymerization .....	10
2.5.1. Initiation .....	11
2.5.2. Propagation .....	13
2.5.3. Termination .....	14
2.6. Free-Radical Polymerization Kinetics .....	17
2.7. Copolymerization .....	19
2.8. Suspension Polymerization .....	20
2.9. Application .....	22

**LIST OF CONTENTS (continued)**

	<b><u>Page</u></b>
<b>3. MATERIALS AND METHOD</b> .....	24
3.1. Materials .....	24
3.2. Synthesis .....	24
3.2.1. Polymerization of Thermally Expandable Microspheres .....	24
3.2.2. Post-processing .....	26
3.3. Characterization .....	26
3.3.1. Surface Morphology .....	26
3.3.2. Core-shell structure analysis .....	26
3.3.3. Particle diameters .....	26
3.3.4. Expansion properties .....	27
3.3.5. Thermal properties .....	27
3.3.6. Chemical properties .....	27
3.3.7. Encapsulated content of core material .....	28
<b>4. RESULTS AND DISCUSSION</b> .....	29
4.1. Effect of Monomer composition .....	29
4.2. Effect of the blowing agent .....	37
4.3. Structural characterization of the microspheres .....	39
4.4. Influence of initiators .....	40
4.5. Thermal property of the particle shell .....	41
<b>5. CONCLUSION AND RECOMMENDATIONS</b> .....	45
<b>REFERENCES</b> .....	47

## LIST OF FIGURES

<b><u>Figure</u></b>	<b><u>Page</u></b>
1.1. Schematic of the expansion of a thermally expandable microsphere (Fredlund, 2011)..1	
2.1. Schematic illustration of the structures of polymer microcapsules. (1) Core-shell structure. (2) Shell-matrix structure. (3) Matrix structure. (4) Polymer-solvent solution. (Huang, 2004).....6	6
2.2. Symbolic representation of suspension polymerization. (a) Monomer droplets formation by mechanical stirring (b) droplet stabilization by suspending agent (Silvério et al., 2015).....20	20
3.1. Experimental setup for preparing thermally expandable microspheres using a round bottle flask by suspension polymerization method.....25	25
4.1. SEM images of particle morphology of poly AN (100 mol %) microspheres.....32	32
4.2. SEM images of particle morphology of poly (AN/MMA) (50/50 mol %) microspheres.....33	33
4.3. SEM images of particle morphology of poly(AN/MMA)(40/60 mol %) microspheres..35	35
4.4. SEM images of particle morphology of poly(AN/MMA)(65/35 mol %) microspheres.37	37
4.5. Thermogravimetric analysis curves of microspheres prepared with different blowing agent.....38	38
4.6. FTIR spectra of the thermally expandable microsphere with poly-(AN-MMA) copolymer shell and n-pentane+isopentane mixture as the core material.....39	39
4.7. Morphology of microspheres prepared with AIBN initiator in absence of inhibitor (NaNO <sub>2</sub> ).....40	40
4.8. Morphology of microspheres when NaNO <sub>2</sub> is added along with AIBN initiator.....41	41
4.9. DTA curves of microspheres with different monomer ratio and blowing agent type ((a) to (e) represent sample T1-T5).....43	43
4.10 Comparison of DTA data of thermally expandable microspheres.....44	44

**LIST OF FIGURES (continued)**

<b><u>Figure</u></b>	<b><u>Page</u></b>
5.1. TEM analysis of thermally expansible microspheres (Sample T-1, Table 1).....	45
5.2. Digital photographs of (a) unexpanded microspheres and (b) expanded microspheres (90-105°C).....	46



**LIST OF TABLES**

<b><u>Table</u></b>	<b><u>Page</u></b>
4.1. Experimental formulas for the polymerization of poly(AN-MMA) thermally expandable microspheres.....	29
4.2. DTA parameters of microspheres with different monomer ratio and blowing agents.....	42

## LIST OF ABBREVIATIONS AND SYMBOLS

<u>Symbols</u>	<u>Descriptions</u>
$A$	Cross-sectional area, $m^2$
$D$	Diffusion coefficient, $m^2/s$
$C$	Concentration of the encapsulated material, $mol/m^3$
$C_o$	Concentration of the medium, $mol/m^3$
$v$	Volume of the microcapsules, $m^3$
$C^t$	Concentration in the microcapsules at time $t$ , $mol/m^3$
$t$	Time, s
$h$	Thickness of the barrier, m
$l$	Diffusion path length, m
$x$	Mole fraction solubility in liquid
$^{\circ}C$	Degree Celsius
$T_g$	Glass-transition temperature, $^{\circ}C$

<u>Abbreviations</u>	<u>Descriptions</u>
ABS	Acrylonitrile-butadiene-styrene
AIBN	2,2'-Azobis(2-methylpropionitrile)
AN	Acrylonitrile
ANFO	Ammonium nitrate fuel oil
DTA	Differential thermal analysis
EPS	Expandable polystyrene
FE-SEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared spectroscopy

**LIST OF ABBREVIATIONS AND SYMBOLS (continued)**

<b><u>Abbreviations</u></b>	<b><u>Descriptions</u></b>
HIPS	High-impact polystyrene
LPO	Lauroyl peroxide
MMA	Methyl methacrylate
MA	Methyl acrylate
MAN	Methacrylonitrile
PAN	Polyacrylonitrile
PMMA	Poly methyl methacrylate
SDS	Sodium dodecyl sulfate
TEM	Transmission electron microscope
TEMs	Thermally expandable microspheres
TGA	Thermal gravimetric analysis
VAc	Vinyl acetate
VDC	Vinylidene chloride

## 1. INTRODUCTION AND OBJECTIVE

Microencapsulation is an essential discipline in the growing technological field, which has advanced applications in recent times (Gouin, 2004). In this process, a continuous film of polymeric material encloses an active substance in solid, liquid or even gaseous form (Benita, 2005). Thermally expandable microspheres (TEMs) are prepared by microencapsulation. In the early 70s, Dow Chemical Co. developed the TEMs, and for the last few decades, it had been further developed by others (Yokomizo et al., 1997; Soane and Houston, 2003). Thermally expandable microspheres are small, spherical polymeric particles, 5-50 $\mu\text{m}$  in diameter, encapsulating a volatile liquid hydrocarbon core with a thermoplastic polymer shell (Jonsson et al., 2006). When the microspheres are exposed to heat above the glass-transition temperature ( $T_g$ ) of the polymer shell, they expand to micro balloons with a 50–100 times larger volume due to the significant internal pressure caused by the gasification of encapsulated hydrocarbon, thereby reducing the density from approximately 1000 kg m<sup>-3</sup> to 30 kg m<sup>-3</sup> (Rheem et al., 2017). Monomers such as acrylonitrile (AN), methyl methacrylate (MMA), vinyl acetate (VAc), vinylidene chloride (VDC) and methyl acrylate (MA) are served as the polymer shell, while low boiling point hydrocarbons such as i-butane, n-pentane, n-hexane, i-octane, petroleum ether are used as blowing agents (Zhou et al., 2017; Hou et al., 2015).

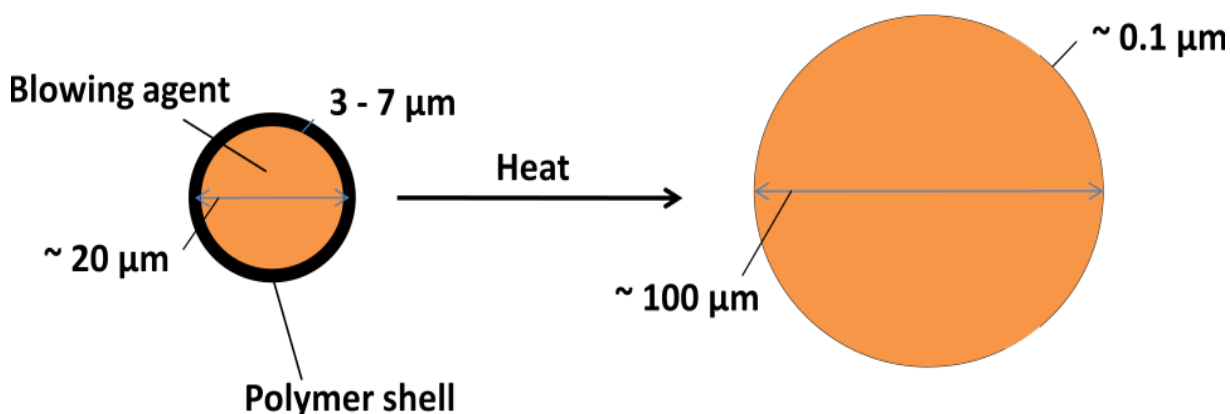


Figure 1.1 Schematic of the expansion of a thermally expandable microsphere (Fredlund, 2011)

Morehouse and Tetreault (1971) developed the thermally expandable microspheres in the late 1960s and early 1970s at Dow Chemicals. Among a few manufacturers, the major producers since the early 1980s are Expancel (part of Eka Chemicals AkzoNobel) from Sweden and Matsumoto Yushi-Seiyaku from Japan.

There are considerable amounts of publications and patents covering different properties of the microspheres and their production, like the composition of the polymer shell (Morehouse and Tetreault, 1971; Yokomizo, 1997; Nordin and Nyholm, 2007; Masuda et al., 2003; Ejiri, 2007; Glorioso et al., 2002), specific hydrocarbons as blowing agents (Kron et al., 2001; Ejiri, 2007), specific suspension stabilizers (Masuda and Tokumura, 2001; Lundqvist, 1996), the reduction of residual monomers (Nakayama and Kida, 1981; Kron et al., 2009) and the expansion techniques for the production of expanded microspheres (Edgren, 1987; Petersen and Svedberg, 1989; Svedberg, 2004). Kawaguchi and Oishi (2004) investigated a set of thermally expandable microspheres to measure the crosslinking efficiencies of dipentaerythritol hexaacrylate on these microspheres and their expandable properties. The contents of the crosslinking agents for optimum expansion were also determined. Kawaguchi et al. (2005) investigated the effects of various additional monomers containing non-nitrile groups on the heat resistance of microspheres containing acrylonitrile and methacrylonitrile. They measured the expandable properties with thermochemical analysis. They investigated the influence of polymer structural properties such as glass-transition temperature, functional free volume and cohesive energy densities to develop heat-resistant microspheres. Kawaguchi et al. (2009) controlled the viscoelasticity by changing the degree of crosslinking of the shell polymer to investigate the expandability and shrinkage behaviour of the microcapsules. Huang (2004) developed a diffusion-viscoelasticity model to investigate the thermal expansion properties of microspheres. The thesis also investigates the effect of the aqueous phase composition on the morphology and expansion properties of these thermally expandable microspheres.

Jonsson et al. (2006) studied the particle morphology of the acrylonitrile (AN)-methacrylonitrile (MAN) copolymer particles with a core/shell structure by investigating the influence of monomer feed ratio and the polymerization temperature. Jonsson et al. (2010) investigated the parameters such as the amount, the boiling point, and the structure of the

blowing agent, which explain the expansion properties of thermally expandable microspheres. Jonsson et al. (2011) synthesized TEMs using different combinations of crosslinkers with varying incorporation rates to manipulate the expansion properties.

Islam et al. (2012) synthesized poly(vinyl acetate - methyl methacrylate) (VAc - MMA) copolymer microspheres using 2,2' -azobis(2,4-dimethyl valeronitrile) (ADMVN), a low-temperature initiator by the suspension polymerization process.

Hou and Kan (2014) prepared thermoexpandable polymeric microspheres with AN and MMA as monomers, i-butane as a blowing agent and ethoxylated trimethylolpropane triacrylate (EOTMTA) as a cross-linking agent by suspension polymerization process and studied the properties of the microspheres.

Rheem et al. (2017) synthesized the microspheres using a variety of initiators with different 10-h half-life decomposition temperatures containing a significant amount of blowing agents with high conversion at low temperatures. They investigated the influence of monomer composition, the initiator type and amount, and polymerization pressure on shell expansion properties, size, and morphology of the microspheres.

Bals et al. (1996) invented encapsulated microspheres to reduce the density of the ammonium nitrate to get a porous prilled product which will be mixed with fuel oil to form the explosive composition known as ANFO. The microspheres will expand to the specified sizes when they are added during the prilling process at a point where the liquid product is divided into droplets.

The correlation between fundamental polymerization parameters and the expansion properties of microspheres are significant to developing microspheres with excellent characteristics. The polymerization parameters which must be studied exclusively includes monomer composition, polymerization temperature, and crosslinking of the polymer shell. Other factors like gas barrier properties of monomer, the balance of softening point and melt viscosity of shell polymer, molecular structure and boiling point of blowing agent are vital to developing TEMs with excellent expansion characteristics (Kawaguchi and Oishi, 2004).

TEMs can be prepared by several methods such as monomer polymerization including conventional emulsion polymerization, dispersion polymerization, suspension polymerization and seed polymerization, and activated swelling method (Yanase et al., 1993; Kondo et al., 1994; Horák et al., 2000; Cocker et al., 1997; Lee et al., 2003; Senna and Lee, 1995; Ugelstad et al., 1992). For the massive production of TEMs, suspension polymerization is the simplest and more suitable method (Yang et al., 2005).

In suspension polymerization, the monomer phase is suspended in a continuous phase (water), containing a stabilizing agent by vigorous stirring. For initiating the chain-growth polymerization, a monomer-soluble initiator is added. Polymerization proceeds within the monomer droplets and consequently forms a three-phase system (monomer/polymer/water). The polymer segment separates from monomer droplets due to the lack of solubility. A major advantage of suspension polymerization is the facilitated removal of heat evolved during the polymerization. (Fried, 2014)

Thermally expandable microspheres have been commercially used for more than 30 years since their development in the early 1970s. Improved thermal properties and capacity of the microsphere are a concern for researchers. There has been a lot of systematic work on expandable microspheres to control the particle size and morphology with publications and patents. However, previous methods often involved polymerization pressure higher than 0.1 MPa, which has disadvantages like a multi-core structure and a low encapsulation ratio of blowing agents (Jalili et al., 2009). In our study, we optimized the polymerization process to synthesize the particles at atmospheric pressure.

The purpose of our study is to prepare various thermally expandable microspheres to compare the effects of monomer composition, core material types, electrolytes, and inhibitors on particle size, morphology, and expansion properties.

## 1. LITERATURE REVIEW

### 2.1 Microencapsulation Technology

We prepared our expandable microspheres by the microencapsulation technique. Microencapsulation is a process in which any compound; solid or liquid, can be encapsulated inside other materials such as a polymer. National Cash Register Company first introduced microencapsulation into the industry 50 years ago in the use of 'no carbon required' copying paper. In this technique, two dyes were enclosed by a clay shell, and a coloured imprint was formed when the shell was ruptured. In the aftermath, the microencapsulation technique has been adopted and applied in industrial and academic areas such as agrochemicals, pharmaceuticals, biotechnology, catalysis, oil and food industries. (Wedlock, 2012)

### 2.2 Microcapsule Structure and Encapsulant Materials

The physical properties of the microcapsule, such as the release characteristics of the encapsulated materials and expansion properties of an expandable particle, largely depends on the structure or morphology of a microcapsule. The structure of a microcapsule can have many variations; therefore, the characterization of the structure of the microcapsule is essential to understand its influence on the properties of the particle.

Figure 2.1 illustrates the four possible structures of the microcapsule. Structure 1 shows a core-shell structure where a continuous core is surrounded by a continuous shell. Structure 2 has a continuous shell where the encapsulated material is scattered through the interior of the microcapsule, thus called 'shell-matrix structure'. The third structure represents a matrix structure where the particles of the encapsulated material are dispersed in a polymer matrix. In the fourth structure, the polymer and the encapsulated material are miscible. The encapsulated material is either dissolved or molecularly dispersed in the polymer matrix, thus forming a uniform single phase. This is the so-called 'polymer-solvent solution'. (Wedlock, 2012)

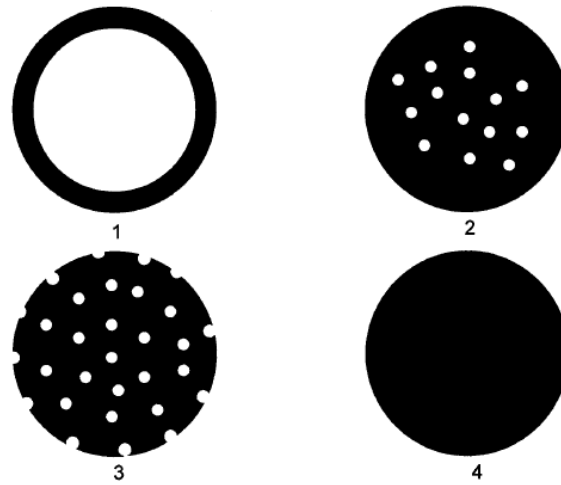


Figure 2.1 Schematic illustration of the structures of polymer microcapsules. (1) Core-shell structure. (2) Shell-matrix structure. (3) Matrix structure. (4) Polymer-solvent solution. (Huang, 2004)

Polymers are appreciably most often used materials for encapsulation though several other materials can be employed to form microcapsules. Although the choice of material essentially depends on the method of microcapsule preparation, the polymers should fulfil the following specifications (Kydonieus, 1980):

- (1) The polymer should have exact molecular weight, glass transition temperature, permeability and molecular structure to fulfil the required release rate of the encapsulated material;
- (2) The polymer should not react with the encapsulated material and should remain stable in the course of general use and storage;
- (3) The polymer should be simply engineered and fabricated into preferred products;
- (4) Biodegradability and biocompatibility characteristics of the polymer is a must for its use in biological and environmental applications.

### 2.3 Theoretical considerations of the release characteristics of encapsulated material

Fick's first law of diffusion explains the diffusion of encapsulated material through the wall of microcapsule:

$$\frac{dc}{dt} = -DA \frac{dx}{dl} \quad (2.1)$$

where  $dc/dt$  is the mass of solute which diffuses in unit time through a cross-sectional area  $A$  with concentration gradient  $dx/dl$ , in the direction  $l$ , and  $D$  is the diffusion coefficient.

Assuming that the medium is an infinite sink and the particles having spherical shape with uniform diameter and size does not change during the dissolution, Equation 2.1 may be rewritten as

$$\frac{dc}{dt} \approx -ADC \quad (2.2)$$

where  $C$  is the concentration of the encapsulated material. Integrating the equation yields

$$\ln(C-C_0) = -DA t + \ln C \quad (2.3)$$

where  $C_0$  is the medium concentration. On the understanding that the area can be estimated, the diffusion coefficient  $D$  can be evaluated by plotting  $\ln(C-C_0)$  versus  $t$ .

The first law can be rewritten to explain the effect of the thickness of the microcapsule wall on the rate of dissolution as

$$\frac{dc}{dt} = -DA \frac{(C-C_0)}{h} \quad (2.4)$$

where  $h$  is the thickness of the barrier. Under sink conditions this equation becomes

$$\frac{dc}{dt} = -KC \quad (2.5)$$

where  $K = AD/Vh$  and  $V$  is the volume of the microcapsules. By Integrating Equation 2.5, we can get a first-order kinetic equation

$$\ln C = \ln C^t - Kt \quad (2.6)$$

where  $C^t$  is the concentration in the microcapsules at time  $t$ .

It is evident from this equation that the rate of release of encapsulated material will decrease with increasing wall thickness of the microcapsule. It is also clear that the increase of particle size will result in the decrease of the rate of release of the encapsulated material.

## **2.4 Methods for Microcapsule preparation**

### **2.4.1 Polymerization Processes**

Heterogeneous polymerization processes such as emulsion polymerization, suspension polymerization and dispersion polymerization processes are employed in microencapsulation technology (Arshady, 1999).

In the emulsion polymerization technique, water is utilized as a heat transfer agent. The monomer used in emulsion polymerization is insoluble in the polymerization medium, but by the aid of a surfactant, it is emulsified in the medium (Arshady 1992; Fried, 2014). By forming large droplets, the hydrophobic monomer molecules are stabilized by the surfactant molecules. The hydrophilic ends of the surfactant molecules point outward, and the hydrophobic ends point inward toward the monomer droplet. Polymerization temperature and the rate of agitation control the size of the monomer droplets (Fried, 2014). The emulsion polymerization technique was widely employed for preparing pigments, fillers and drug encapsulation (Erdem et al., 2000; Arshady, 1999).

The term suspension polymerization describes a process in which both monomer and initiator are insoluble in the polymerization medium, but the initiator is soluble in monomer. The substantial aim of suspension polymerization is to form a uniform dispersion of monomer droplets in the polymerization medium with the presence of a stabilizer that controls the coalescence of the monomer droplets in the course of polymerization to produce solid beads of the same spherical size (Vivaldo-Lima et al., 1997).

The monomer and the initiator used in dispersion polymerization are both soluble in the polymerization medium, although the resulting polymer is poorly soluble in the medium. The monomer is emulsified in the medium by using a surfactant. The monomer may form droplets or soap-coated micelles in the mixture, which is controlled by the nature and concentration of the emulsifier. (Arshady, 1992)

Suspension and dispersion polymerization processes are employed in the microencapsulation of solid particles where the polymer encapsulate the solid core. At times the core substance is dissolved or dispersed in the monomer accompanied by polymerization to accomplish encapsulation. The higher affinity of the solid substance for the monomer phase over that of the polymerization medium is vital for the encapsulation process. (Huang, 2004)

#### **2.4.1.1 Interfacial polymerization**

Interfacial polymerization is based on the interfacial polycondensation polymerization technique, which is employed to produce synthetic fibers (Nelson, 2013). In this process, two monomers having a high partition coefficient of opposite values are polymerized at the interface of two immiscible phases. The formation of a two-phase droplet suspension is essential to prepare such microcapsules. Shell wall is formed at the surface of the droplets or particles of dispersed core material by rapid polymerization of monomers. The solubility of the polycondensates controls the morphologies of the microcapsule. (Huang, 2004)

### **2.4.2 Physicochemical Methods**

#### **2.4.2.1 Emulsification/solvent evaporation**

Microencapsulation by emulsification/solvent evaporation involves dissolution or dispersion of the material to be encapsulated, the active, in a polymer solution. The droplets containing polymer, active ingredient and solvent are then dispersed in an immiscible medium on the addition of an emulsifier. A suspension of core containing microcapsules is formed by

applying heat, vacuum or allowing evaporation at room temperature. The microcapsules are then separated by filtration or centrifugation.

In the emulsification/solvent evaporation microencapsulation technique, the particle size is controlled by the mixing conditions. Benita *et al.* observed that the particle size decreases exponentially with mixer speed (Benita *et al.*, 1984). By using baffles in the mixing tank, vortex formation can be avoided, which leads to the formation of aggregates.

#### **2.4.2.2 Coacervation/Phase separation**

Coacervation is considered as one of the oldest and most widely used techniques for forming microcapsules based on gelatin, cellulose derivatives and synthetic polymers by phase separation (Burgess and Carless, 1985; Nimmannit and Suwanpatra, 1996). Phase coacervation can be divided into the following two groups: i) simple coacervation and ii) complex coacervation. Simple coacervation involves the use of one colloidal solute such as gelatin or chitosan, whereas two oppositely charged colloids such as gelatin and acacia, both of which are soluble in aqueous media, interact to form an aqueous polymeric solution in complex coacervation. (Deveci and Basal, 2009)

In microencapsulation by coacervation, the core material (hydrophobic) is dispersed into an aqueous polymer solution of a surface-active hydrocolloid (1-10%) at 40-50°C under continuous agitation. The addition of a non-solvent or changing pH or temperature lowers the solubility of the hydrocolloid resulting in precipitation of the hydrocolloid onto the dispersed droplets. In the case of complex coacervation, the polymer-polymer complex is induced by the addition of a second hydrocolloid. The microcapsules are stabilized by adding a cross-linking agent such as formaldehyde or glutaraldehyde. (Nelson, 2013)

### **2.5 Free Radical Polymerization**

The independently-existing chemical species which are normally highly reactive with short lifetimes and possess an unpaired electron are called free radicals. Like other chain-growth

polymerizations, in free-radical polymerization, by addition of monomer to a terminal free-radical reactive site known as an active centre, each polymer molecule is grown. The active centre is transferred to the newly-created chain end by consequent addition of each monomer. Free-Radical polymerization is widely practised for the preparation of polymers from a large number of unsaturated monomers like ethylene ( $\text{CH}_2=\text{CH}_2$ , the simplest olefin),  $\alpha$ -olefins ( $\text{CH}_2=\text{CHR}$ , where R is an alkyl group), vinyl compounds ( $\text{CH}_2=\text{CHX}$ , where X=Cl, Br, I, alkoxy, CN, COOH, COOR,  $\text{C}_6\text{H}_5$ , etc., atoms or groups) and conjugated diolefins [e.g., butadiene,  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ , and isoprene,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$ ]. In free-radical polymerization, the reaction can be divided into three principal steps: initiation of the active monomer, propagation or sequential addition of monomers resulting in the growth of the active (i.e., free-radical) chain, acquiring the polymer by the termination of the chain.

### 2.5.1 Initiation

In a free-radical polymerization, initiation consists of two steps: (i) dissociation and (ii) association and free-radical active centre is created at this step. In dissociation step two radical species are formed from an initiator followed by association step in which addition of one of the free radicals to a single molecule of monomer occurs. The free-radical initiator species ( $\text{I}\cdot$ ) formed from the dissociation of the initiator ( $\text{I-I}$ ) can be represented as follows:

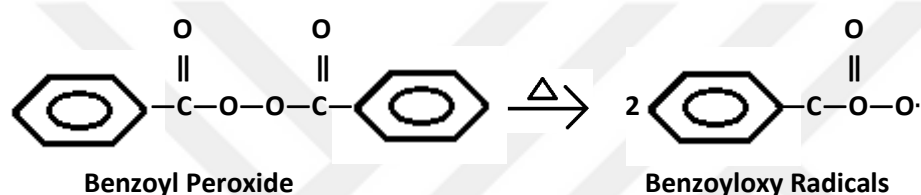


where  $k_d$  is the dissociation rate constant. The dependence on temperature of the dissociation rate constant can be defined by Arrhenius Equation as follows:

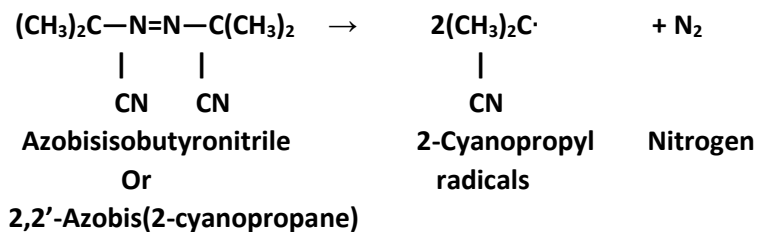
$$k_d = A \exp(E_a / RT) \quad (2.8)$$

where  $A$  in eq. ( ) is a rate parameter and  $E_a$  is the activation energy for dissociation.

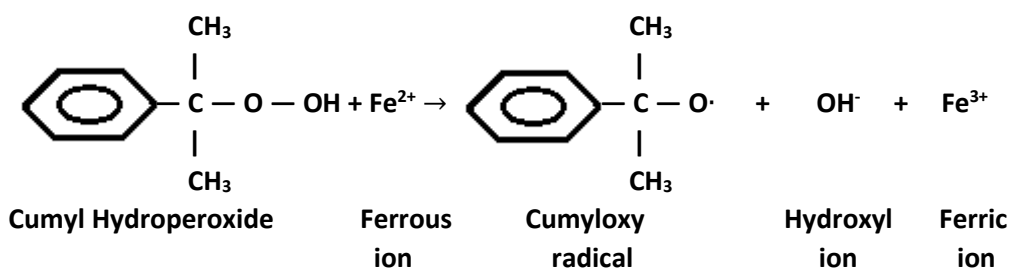
Free radicals can be formed by two principal ways: (i) homolytic scission (i.e. homolysis) of a single bond, and (ii) single electron transfer to or from an ion or molecule (e.g. redox reactions). By the application of heat ( $\Delta$ ) homolysis can be effected and in the convenient temperature range of 50-100°C, peroxide (-O-O-) or azo (-N=N-) linkages containing compounds undergo thermolysis. Photolysis (usually ultraviolet) can also be used for homolytic scission. Heat or radiation, such as UV or  $\gamma$ -irradiation breaks the labile bond of the initiator. For example, benzoyl peroxide dissociates into two identical benzoyloxy radicals.



Similarly, 2,2'-azobis(isobutyronitrile) (AIBN), an important member of the family of azo (R-N=N-R) compounds thermally decomposes into nitrogen gas and two cyanoisopropyl radicals (R•) as



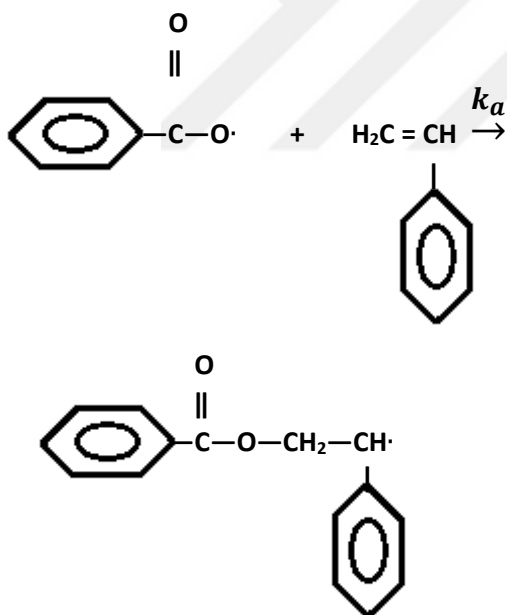
For polymerizations at low temperatures, redox reactions are often used. An example of redox reaction to form free-radical is given below



In the addition step, a monomer molecule (M) is attached to the initiator radical which may be represented as



where  $k_a$  is the rate constant for monomer association. For example, in benzoyl peroxide initiated polymerization reaction of styrene, the addition occurs as

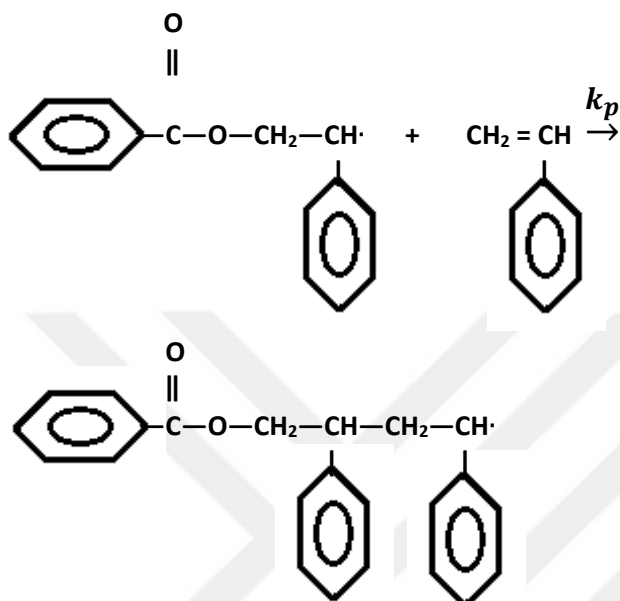


### 2.5.2 Propagation

In the propagation step, the polymer chain is grown up by the sequential addition of the additional monomer units to the initiated monomer species as



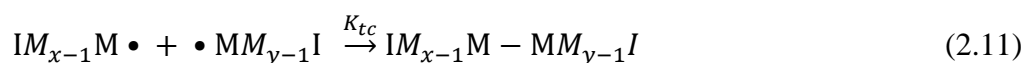
where  $k_p$  is the propagation rate constant. The first propagation step for benzoyl peroxide initiated styrene addition is



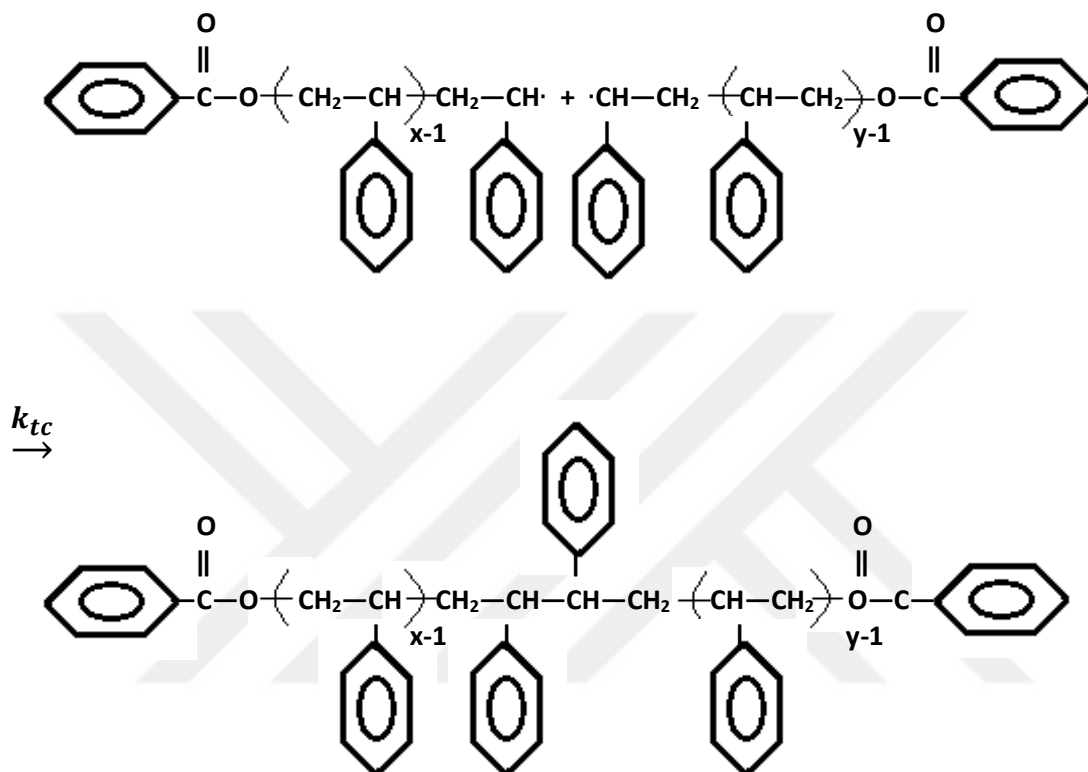
The addition of each monomer typically requires time in the order of millisecond. Therefore within a few seconds several thousand additions can take place.

### 2.5.3 Termination

With an actual termination process, the propagation step stops. Termination step involves bimolecular reaction of growing polymer chains by two common mechanisms: combination and disproportionation. In combination mechanism, termination occurs through the formation of a covalent bond between the two combining radical chains giving one terminated chain of degree of polymerization  $x+y$  where two propagating radical chains meet at their free-radical ends having arbitrary degrees of polymerization ( $x$  and  $y$ ). Termination by combination mechanism can be represented by following reaction:



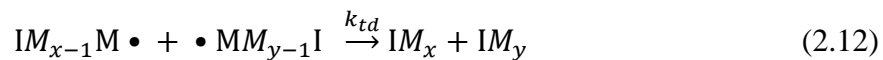
where  $k_{tc}$  is the termination rate constant. For example, termination of the styrene polymerization by combination mechanism gives the following reaction:



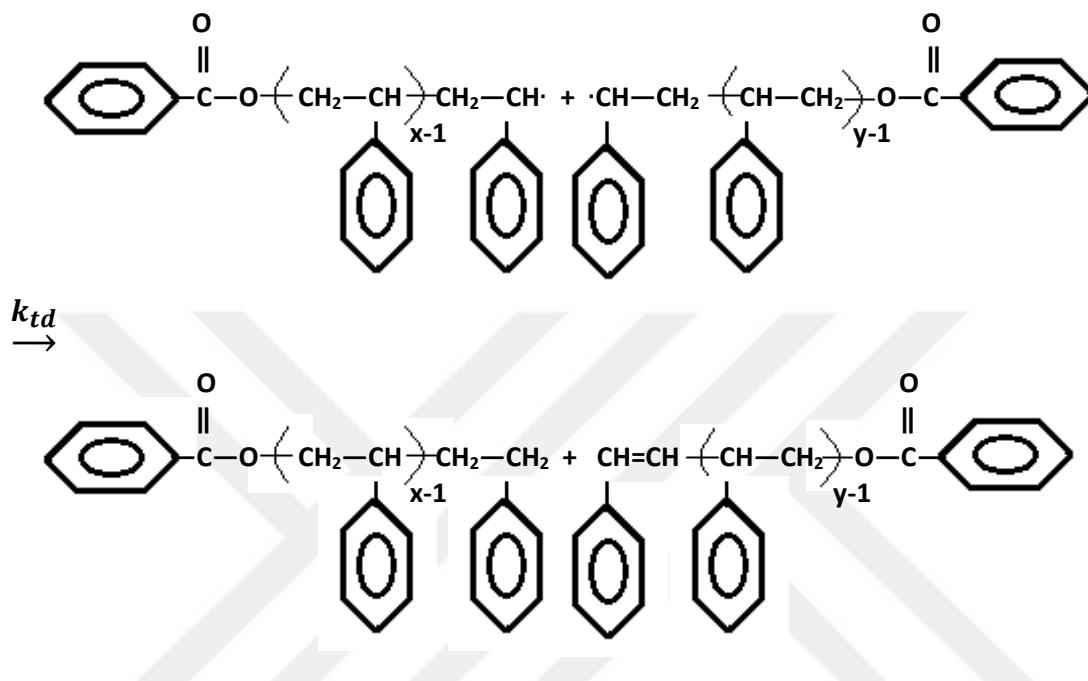
Note that the termination by combination results in a 'head-to-head' linkage of styrene units at the combination site.

In disproportionation mechanism, termination occurs to give two terminated chain where one polymer is formed with a saturated end-group while the other with an unsaturated end-group. Also disproportionation yields polymer molecules with initiator fragments at only one end whereas in termination by combination, the chain contains free-radical group of the initiator molecule at both ends.

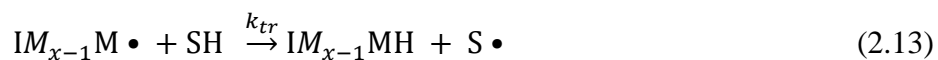
The following reaction illustrates termination by disproportionation as



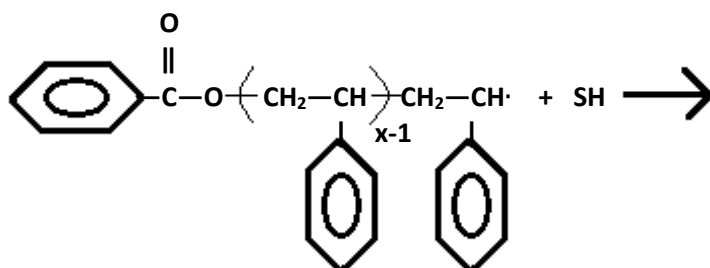
where rate is the rate constant,  $k_{td}$ . Termination by disproportionation in case of styrene polymerization initiated by benzoyl peroxide gives the following reaction:

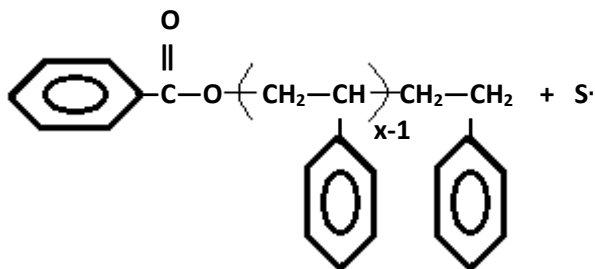


Chain transfer is another mechanism of termination which occurs by abstraction of hydrogen atom or other species from an initiator, monomer, polymer, or solvent molecule. This process can be illustrated as follows:



where SH represents a solvent with an abstractable hydrogen atom and  $k_{tr}$  is the rate constant for the chain-transfer reaction. In the case of styrene polymerization with benzoyl peroxide initiation, termination by chain transfer occurs as





## 2.6 Free-Radical Polymerization Kinetics

In free-radical polymerization, the overall rate of polymerization ( $R_o$ ) is simply the rate of chain propagation ( $R_p$ ), as obtained from eq. 2.10

$$R_o \equiv R_p = k_p [IM_x^\bullet][M] \quad (2.14)$$

The assumption that all steps have equal reactivity can be made by this statement. The value of the radical concentration,  $[IM_x^\bullet]$  to determine the polymerization rate is unknown. This difficulty can be overcome by relating the radical concentration to monomer or initiator concentrations assuming a steady-state concentration of the total radical population during the polymerization process. As in the termination step the radicals are consumed which were formed in initiation step, therefore the steady-state condition may be expressed by

$$R_i \equiv R_t \quad (2.15)$$

As dissociation of the initiator is the slower step, the overall rate of reaction of initiation is controlled by this step, therefore it is expressed as

$$R_i = \frac{d[I^\bullet]}{dt} = 2k_d[I] \quad (2.16)$$

Initiator radicals contribute to chain propagation are only considered in the expression of the rate of polymerization. Therefore the rate expression can be revised with the introduction of the fraction of effective initiator radicals as

$$R_i = \frac{d[I\bullet]}{dt} = 2fk_d[I] \quad (2.17)$$

Simplification of termination step by considering only combination and disproportionation, it can be expressed as



where P represents the deactivated polymer and the individual summation of termination rate constants for combination and disproportionation (i.e.,  $k_t = k_{tc} + k_{td}$ ) is the termination rate constant,  $k_t$ .

The termination rate equation can be written in the similar fashion as the time rate of decrease in radical concentration

$$R_t = - \frac{d[IM_x \bullet]}{dt} = 2k_t[IM \bullet]^2 \quad (2.19)$$

The expression for the radical concentration can be obtained by applying steady-state assumption, i.e. the rates of initiation and termination are equal and expressed as

$$[IM_x \bullet] = \left( \frac{fk_d}{k_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} \quad (2.20)$$

This way the rate of polymerization can be expressed by the following equation:

$$R_o = k_p \left( \frac{fk_d}{k_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} [M] \quad (2.21)$$

The number-average degree of polymerization, which is the ratio of the rate of propagation to the rate of termination ( $\bar{X}_n$ ) can be expressed at steady-state by following equation (Fried, 2014)

:

$$\bar{X}_n = \frac{k_p[M]}{2(k_t f k_d [1])^{\frac{1}{2}}} \quad (2.22)$$

## 2.7 Copolymerization

The simultaneous polymerization of two or more monomers (or copolymerization) was investigated in 1910. The discovery of the production of elastomers from copolymers of olefins and dienes rather than either polyolefins or polydienes alone paved the way to the concept of copolymerization. The vast majority of commercially important polymers are produced by copolymerization of monomers with different properties. The diversification of the compositions of copolymers from only a small percentage of one component to comparable proportions of both monomers permits the production of a variety of end uses polymer products with vastly different properties. Relative reactivity of each monomer or, more precisely, the reactivity of the propagating radical towards the monomers in the system affects the polymer composition. In a copolymerization of two monomers ( $M_1$  and  $M_2$ ), four separate propagation steps and the associated rate equations can be considered.

Reaction	Rate Equation	
$M_1 \cdot + M_1 \rightarrow M_1 \cdot$	$K_{11}[M_1 \cdot][M_1]$	
$M_1 \cdot + M_2 \rightarrow M_2 \cdot$	$K_{12}[M_1 \cdot][M_2]$	(2.23)
$M_2 \cdot + M_1 \rightarrow M_1 \cdot$	$K_{21}[M_2 \cdot][M_1]$	
$M_2 \cdot + M_2 \rightarrow M_2 \cdot$	$K_{22}[M_2 \cdot][M_2]$	

At steady state, it is assumed that the rates of generation and consumption of  $M_1\cdot$  and  $M_2\cdot$  radicals are equal. Therefore by equating the rate of conversion of  $M_1\cdot$  to  $M_2\cdot$  that of conversion of  $M_2\cdot$  to  $M_1\cdot$  from Equation 2.23 gives the following equation

$$K_{21}[M_2\cdot][M_1] = K_{12}[M_1\cdot][M_2] \quad (2.24)$$

The rates of disappearance of monomers  $M_1$  and  $M_2$  can be obtained by considering the consumption of the monomers from their individual propagation steps.

$$\frac{-d[M_1]}{dt} = K_{11}[M_1\cdot][M_1] + K_{21}[M_2\cdot][M_1] \quad (2.25)$$

$$\frac{-d[M_2]}{dt} = K_{12}[M_1\cdot][M_2] + K_{22}[M_2\cdot][M_2] \quad (2.26)$$

By dividing Equation 2.25 by Equation 2.26 we obtain the relative change in the co-monomer composition in the form

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] r_1[M_2] + [M_2]}{[M_2] [M_1] + r_2[M_2]} \quad (2.27)$$

## 2.8 Suspension polymerization

Polymer particles are produced on an industrial scale by suspension polymerization technique which is one of the major heterogeneous polymerization techniques where all the reactants, including monomers, initiators, and solvents, are mutually insoluble (Arshady, 1992; Yuan, 1991). In the early 1900s, suspension polymerization technology was developed in Germany in the pursuance of producing synthetic rubber (Hofman and Delbruck, 1909; Gottlob, 1915).

In suspension polymerization, the monomer is dispersed as a liquid in small droplets containing monomer soluble initiator into polymerization medium (continuous phase), an agitated stabilizing medium containing small amounts of suspension and dispersion agents along with water (Figure 2.2). The monomer droplets work as a small bulk polymerization reactor and directly produce polymer particles. The polymer particles produced by suspension

polymerization can, in principle in size range from about 100 nm up to about 1-2 mm or larger (Arshady, 1992).

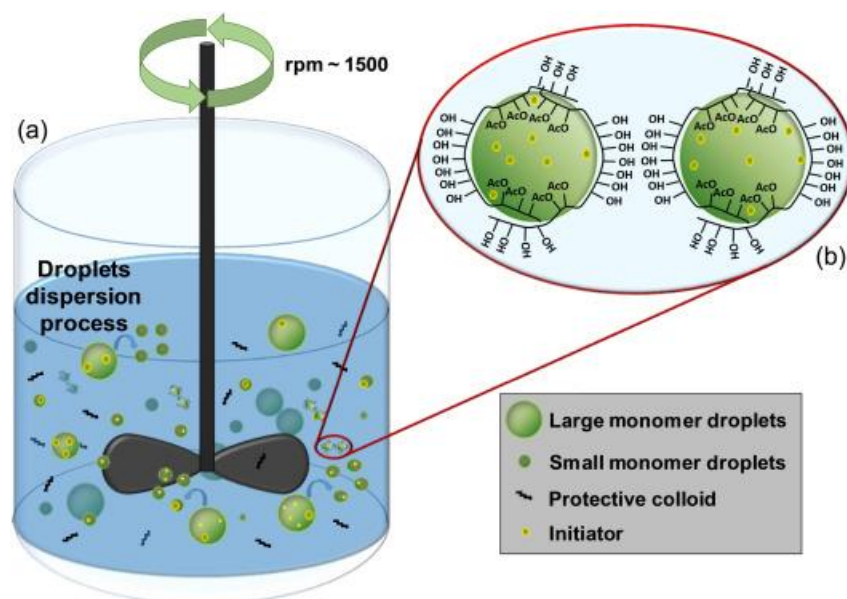


Figure 2.2 Symbolic representation of suspension polymerization. (a) Monomer droplets formation by mechanical stirring (b) droplet stabilization by suspending agent (Silvério et al., 2015)

A variety of important commercial resins are manufactured by suspension polymerization, including poly- (vinyl chloride), styrene resins (poly(acrylonitrile-butadiene-styrene) (ABS), expandable polystyrene (EPS), high-impact polystyrene (HIPS), styrenic ion-exchange resins), poly(methyl methacrylate) and poly(vinyl acetate) (Yuan et al., 1991).

Suspension polymerization has numerous attractive features compared with the other polymerization processes (bulk, solution, and emulsion). The continuous phase: water, used as a heat-transfer medium, is more cost-effective than the organic solvents used in most solution polymerization processes. Because of the high specific heat and the low dispersion viscosity of water, removing the excessive heat of polymerization presents minimal problems; therefore, it provides better control of temperature in the organic droplets, which can be maintained throughout the process compared to bulk- or solvent polymerizations. The final product is

obtained as particle form, and separation and purification are relatively easier than emulsion polymerization. (Vivaldo-Lima et al., 1997)

Suspension polymerization processes are categorized into three different types. In bead suspension polymerization, the monomer dissolves the polymer; therefore, the viscosity of the monomer droplets increases during polymerization. In powder suspension polymerization, the polymer is not dissolved by its monomer; therefore, precipitation of polymers occurs within each monomer droplet, and opaque, irregular grains or powders are finally formed. (Yuan et al., 1991)

The bulk polymerization rate equation can be applied to a suspension polymerization system assuming that the polymerization is subject to a free-radical mechanism, at low to moderate conversions:

$$R_p = k_p \left( \frac{fk_d}{k_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} [M] \quad (2.28)$$

Suspension polymerization kinetics can be explained in three stages. Depending on the amount of agitation and concentration of suspending agent, the droplet size is small and the particle size distribution (PSD) is narrow in stage 1. At this stage, the suspension is quite stable and the droplet population dynamics are fast. At 20-35 % conversion, the 2<sup>nd</sup> stage starts; the droplets become highly viscous and viscoelastic therefore the breakage and coalescence rates decrease. The prolongation of stage 2 or domination of coalescence will result in a broader particle size distribution or even agglomeration. Higher conversions are observed and the particles become solid in stage 3. The propagation rate decreases as monomer diffusion limitations become evident. (Huang, 2004)

## 2.9 Application

The unique expansion capability of microspheres makes them extensively useful in a wide variety of industrial applications. Their scope of application includes coating, printing inks, 3D wallpaper, plastics, textiles, extrusion, injection moulding, sealants, lightweight fillers and

blowing agents. TEM is also used as underbody coatings, tires, and composite materials in the automotive industry, single-use pumps or valves in microfluidic systems and sacrificial templates in the production of foamed ceramics (Jonsson, 2010; Jonsson et al., 2010). Various expandable thermoplastic microspheres are commercially available under the trademarks Expancel™ by Nouryon, Advancell™ by Sekisui Chemical, Dualite™ by Chase Corporation and are used in different applications as a foaming agent.

Hollow microspheres, the expanded state of the thermally expandable microsphere, can be used as fillers as an alternative to conventional fillers (e.g., silicates, clays). Cell coalescence, time and temperature-dependent gas diffusion, and unequal cell growth are some of the problems allied with the foaming process, which can be solved by using these microspheres. Printing inks and paints prepared with added hollow particles provide a smoother surface finish, lower viscosity and better applicability. (Huang, 2004)

Ammonium nitrate fuel oil (ANFO) is the most common commercially available explosive used in the mining industry. ANFO explosive is typically a stoichiometric mixture of porous ammonium nitrate (94.5%) and mineral oil (5.5 %), where ammonium is the primary ingredient (Zygmunt and Buczkowski, 2007). The explosive characteristics of ammonium nitrate closely bound the explosive properties of ANFO as ammonium nitrate solely has got the explosive properties in such a mixture. Highly porous ammonium nitrate improves the efficiency of ANFO action. The physical features and chemical composition of ammonium nitrate prills may influence the detonation parameters of the explosive to a high degree (Zygmunt and Buczkowski, 2007). The pore structure of low-density ammonium nitrate enables them to absorb the required fuel oil. A dilute aqueous solution of ammonium nitrate is cooled down in a prilling tower wherein liquid droplets are converted to the solid low-density ammonium nitrate prills. The voids in the structure of ammonium nitrate permit liquid hydrocarbon fuel to penetrate and become intimately associated with the ammonium nitrate (Bals et al., 1996). Thermally expandable microspheres are used to reduce the density of the prilled ammonium nitrate during the prilling process at a point where the liquid product is divided into droplets by expanding their size to a specified level (Bals et al., 1996).

## 2. MATERIALS AND METHOD

### 3.1 Materials

All the reagents except a few were purchased from well-known commercial chemical suppliers and were used as received. Acrylonitrile (AN; stabilized with hydroquinone monomethyl ether, Sigma-Aldrich), methyl methacrylate (MMA; contains  $\leq 30$  ppm MEHQ as inhibitor), methacrylonitrile (MAN; 97.6%, LGC), vinyl acetate (VAc; 99%, Aldrich), 2,2'-Azobis(2-methylpropionitrile) (AIBN; 98% , Sigma-Aldrich), lauroyl peroxide (LP; 97% , Sigma-Aldrich), 2-Methylbutane ( anhydrous,  $\geq 99\%$  , Sigma-Aldrich), pentane (anhydrous,  $\geq 99\%$  , Sigma-Aldrich), methylcyclopentane ( $C_6H_{12}$ ;  $>98\%$ , Merck), sodium 2-ethylhexyl sulfate (~50% in water, Sigma-Aldrich), sodium dodecyl sulfate (SDS;  $\geq 99\%$ , Sigma-Aldrich), hydrochloric acid (HCl; fuming 37%, Isolab), sodium chloride (NaCl;  $\geq 99.5\%$ , Isolab), sodium hydroxide (NaOH; pellets, Supelco), magnesium chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ ; Carlo Erba).

### 3.2 Synthesis

#### 3.2.1 Polymerization of Thermally Expandable Microspheres

TEMs were prepared by suspension polymerization (Figure 3.1) according to the previous literature with some optimization of the polymerization conditions (Jonsson et al., 2006; Yi et al., 2021). Aqueous phase: A magnesium hydroxide dispersion was prepared by thoroughly mixing a NaOH solution (0.60g NaOH (s) in 15g deionized water) with a  $MgCl_2$  solution (2.0g  $MgCl_2 \cdot 6H_2O$  (s) in 15g deionized water) in a flask under 400 rpm magnetic stirring for about 30 min. 1g NaCl (s) was added as dispersion aid followed by the addition of 0.4g of a 1wt% solution of sodium 2-ethylhexyl sulfate (aq) as a dispersing agent. Oil Phase: In another flask, the organic phase was prepared with monomers consisting of 4g of acrylonitrile (AN), 4g of methyl methacrylate (MMA), followed by the addition of 0.09g azobisisobutyronitrile (AIBN). The flask was sealed properly and was put in an ice-water

mixture. Subsequently, a 3.5g mixture of n-pentane and isopentane (ratio 1:1) as the core material was dripped into the organic phase, and this phase was mixed for about 25 min under magnetic stirring at 400 rpm to obtain the transparent liquid of the oil phase. Finally, the aqueous phase and oil phase were mixed in a flask, and the mixture was sheared under cooling condition using a homogenizer (IKA Ultra Turrax T25 Basic) at the homogenization rate of 11000 rpm for about 60s. The suspension was transferred into a two-neck flask, and oxygen was removed from the flask by purging with nitrogen. The flask was immediately sealed (Suba-seal, Sigma-Aldrich), and the polymerization was conducted using a magnetic stirrer (MR Hei-Standard) with a water bath at 60°C and reacted for about 20 h under magnetic stirring at 350-400 rpm. After finishing the polymerization, the resulting slurry was cooled to room temperature.



Figure 3.1 Experimental setup for preparing thermally expandable microspheres using a round bottle flask by suspension polymerization method

### **3.2.2 Post-processing**

By acidifying the  $P^H$  of the solution to 3-4 under stirring using diluted hydrochloric acid, the suspending agent was removed from the particles. The products were washed thoroughly with distilled water and filtered with filter paper. The microcapsules were dried in an oven for more than 24 h at 25-30°C. Finally, a 112 $\mu$ m sieve was used to remove agglomerates and larger particles from the final product.

## **3.3 Characterization**

### **3.3.1 Surface Morphology**

The particle morphology of the microsphere was analyzed using a Hitachi Regulus 8230 field emission scanning electron microscope (FE-SEM). The thermally expandable microspheres were coated using a Leica EM ACE600 coating device with a thin layer of gold before the analysis.

### **3.3.2 Core-shell structure analysis**

Transmission electron microscope (Hitachi HT7800) was used to observe the core-shell structure of the microspheres. The microspheres were mixed with anhydrous ethanol for sonication using ultrasonic bath. The core-shell structure was observed by dispersing the resulting suspension on a copper mesh and analyzing it using the TEM device.

### **3.3.3 Particle diameters**

Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to observe the particle diameters. Microspheres were chosen randomly and the particle diameter was analyzed from the microscope photograph.

### **3.3.4 Expansion properties**

A drying oven was used to measure the expansion temperature and expansion ratio, which represent the expansion properties of thermally expandable microspheres. 0.5 ml dried microsphere powder was placed in a 10ml measuring cylinder, which then heated in a drying oven from 80°C to 110°C temperature and maintained for about 4 min. When the microspheres began to balloon at a specific temperature, that temperature was specified as expansion temperature. The expansion ratio was determined from the ratio of the microspheres volumes before and after heating.

### **3.3.5 Thermal properties**

A differential thermal analyzer (DTA, Perkin Elmer Diamond TG/DTA) was used to determine the glass transition temperature ( $T_g$ ) of the microspheres. 3.40 mg of dried microsphere was placed in an aluminum crucible. The DTA instrument was used to analyze the microspheres in a nitrogen atmosphere with an initial and final temperature set as 20°C and 300°C respectively at a heating rate of 10°C/min.

### **3.3.6 Chemical properties**

Fourier transform infrared (FTIR) spectroscopy was used to characterize the chemical structure and composition of the microspheres. A Perkin Elmer Spectrum Two FTIR spectrometer was used to detect the infrared absorption spectra of microspheres. A certain amount of potassium bromide was mixed with a small amount of sample and then pressed into a transparent tablet. The scanning was conducted with the FTIR instrument with the wavenumber ranging from 400 to 4000  $\text{cm}^{-1}$ .

### **3.3.7 Encapsulated content of core material**

Thermal gravimetric analysis (TGA, Perkin Elmer STA 8000) was used to determine the encapsulated content of the core material for microspheres as well as to examine polymer decomposition. Excess moisture and residual monomers were removed from the samples before conducting the analysis by drying them with care as excessive heat can affect the hydrocarbon content. The samples were added to a crucible and thermally weighted using a thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10°C/min with initial and final temperatures being 20°C and 525°C, respectively. The encapsulated content of core material was calculated from the per cent weight loss of polymer microspheres using the thermogravimetric curve.

### 3. RESULTS AND DISCUSSION

#### 4.1 Effect of Monomer composition

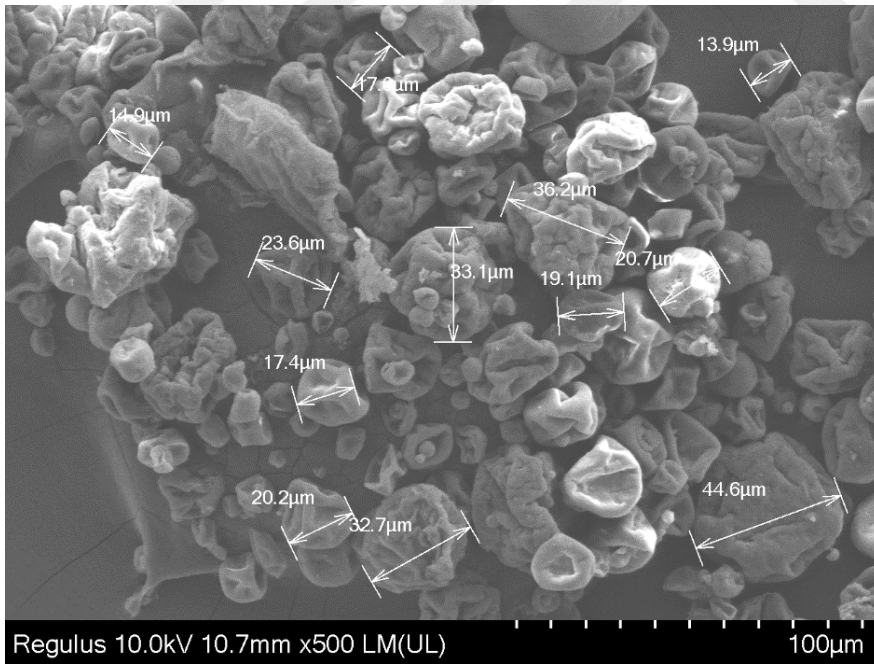
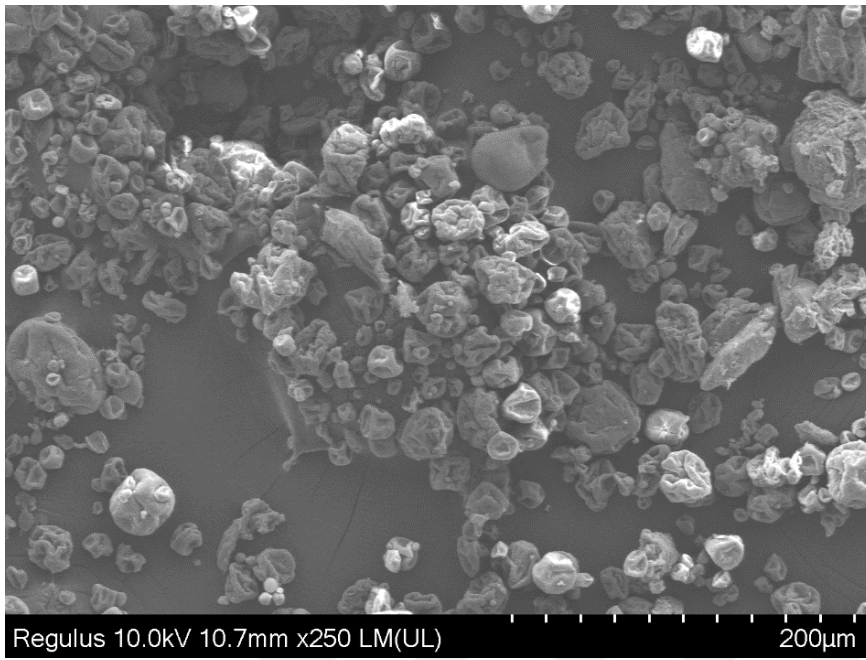
Table 4.1 shows different experimental formulas for polymerization with a different monomer ratio of AN and MMA. Figure 4.1 shows that when monomer feed composition is 100 mol% AN, agglomerates are formed. Uniform molecular chain segment, compact structure, high degree of crystallinity, and high glass transition temperature make AN highly rigid, weakly ductile and flexible homopolymer (Huang et al., 2004). When heated up to 200°C, the homopolymer shell of AN (100 mol%) microspheres did not expand. The pressure generated by the gasified hydrocarbon was not sufficient to overcome the rigidity of the polymer shell. Acrylonitrile exhibits a certain solubility in water, would enter the aqueous phase, and secondary particles would form on the droplet surface during polymerization (Ma et al., 2004).

Table 4.1 Experimental formulas for the polymerization of poly(AN-MMA) thermally expandable microspheres

Run (sample code)	AN (mol %)	MM A (mol %)	Blowing agent (wt %)	Initiator	NaCl (g)	Expa- nsion ratio	Expansion temperature (°C)
1	100	0	i-pentane 20	LPO	0	-----	-----
2 (T-1)	50	50	n-pentane+i- pentane (1:1) 30	AIBN	1	3.33	90-110
3	50	50	n-pentane	AIBN	1	-----	-----

Table 4.1 continued

Run (sample code)	AN (mol %)	MM A (mol %)	Blowing agent (wt %)	Initiator	NaCl (g)	Expa- sion ratio	Expansion temperature (°C)
4	50	50	i-pentane	AIBN	2		
5	50	50	n-pentane+i- pentane (4:1) 30	AIBN	5.5	-----	-----
6	60	40	n-pentane+i- pentane (1:1) 30	AIBN	0.75	-----	-----
7	70	30	n-pentane+i- pentane (1:1) 30	AIBN	0.75	----- -	-----
8 (T-2)	50	50	n-hexane+heptane (1:1) 30	AIBN	1	----- -	----- --
9	50	50	n-pentane+i- pentane (1:1) 30	LPO	1	----- -	----- -
10 (T-3)	50	50	n-hexane 30	AIBN	0	1.3	140-150
11 (T-4)	40	60	n-hexane+n-octane (1:1) 30	AIBN	0	-----	-----
12 (T-5)	65	35	n-hexane 30	LPO	0		



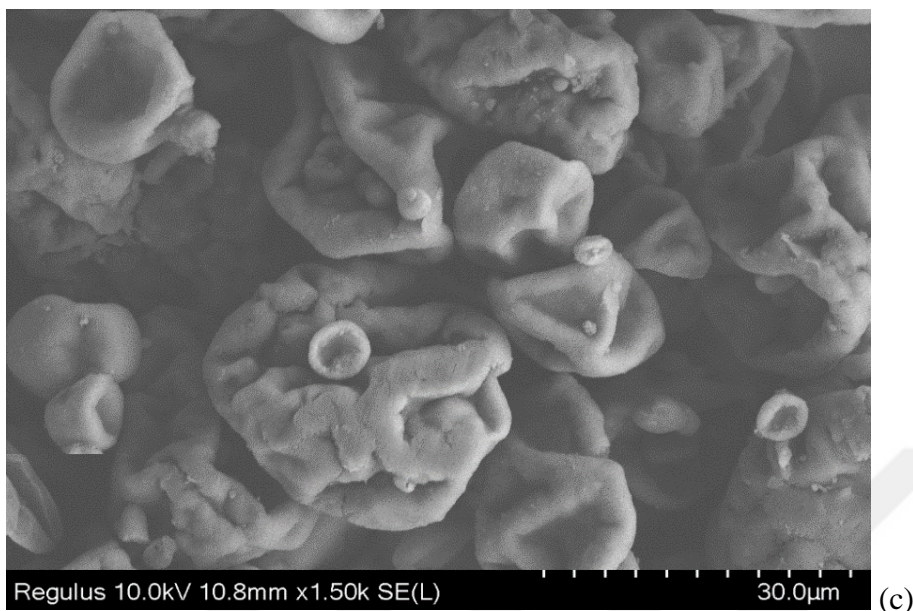
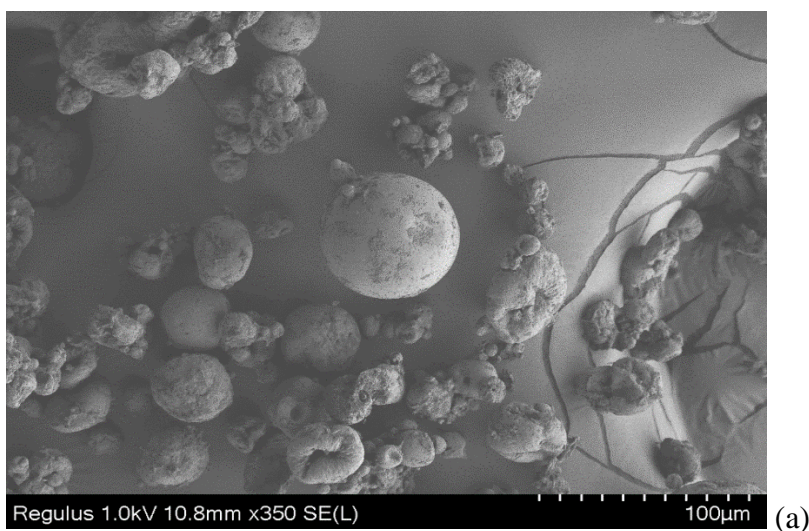


Figure 4.1. SEM images of particle morphology of poly AN (100 mol %) microspheres. Zoom-in images (a: scale bar =200 $\mu$ m, b: scale bar =100 $\mu$ m (with particle diameter), c: scale bar = 30 $\mu$ m)

Figure 4.2 shows the morphology of AN and MMA copolymer microspheres when AN was 50 mol % substituted by MMA. The flexibility of the AN and MMA copolymer increased in comparison to AN homopolymer due to the irregularity of the molecular chain of the copolymer. The expansion property of the microsphere was improved due to the partial substitution of MMA for AN, and the copolymer shell expanded when heated at 105°C.



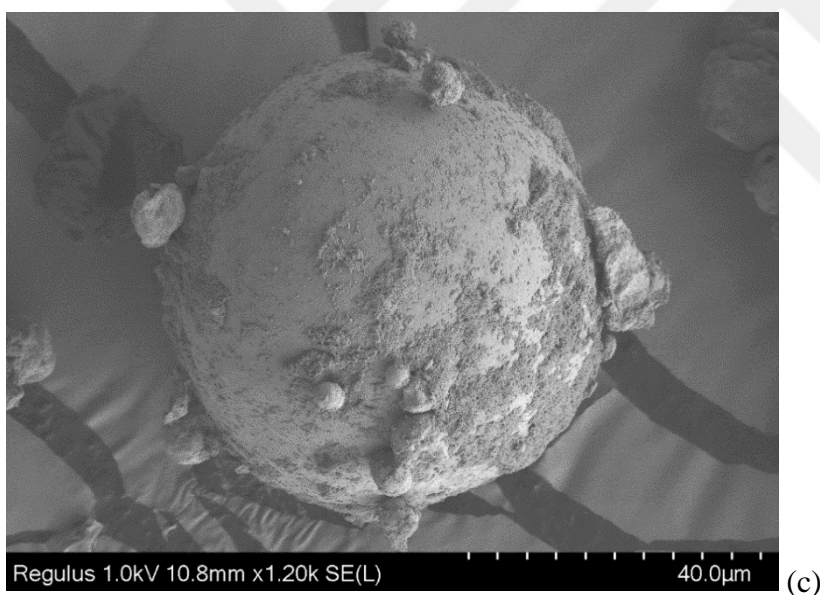
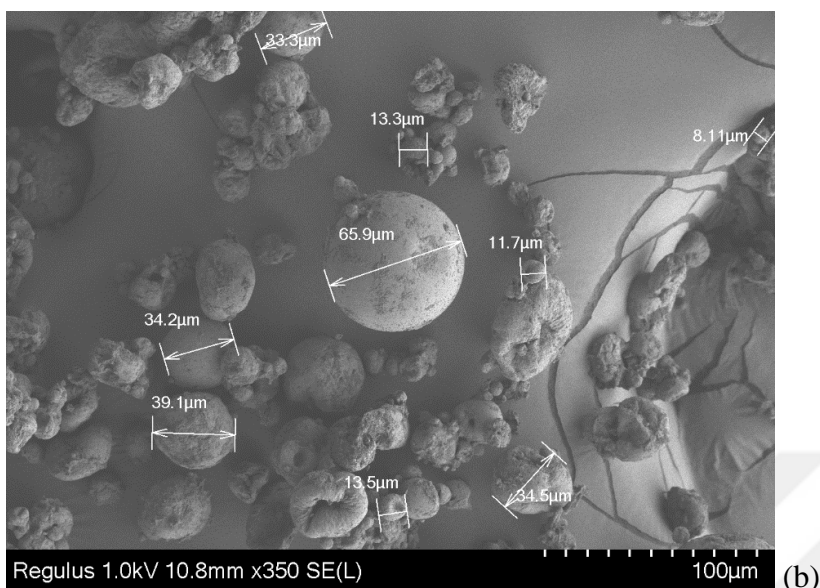


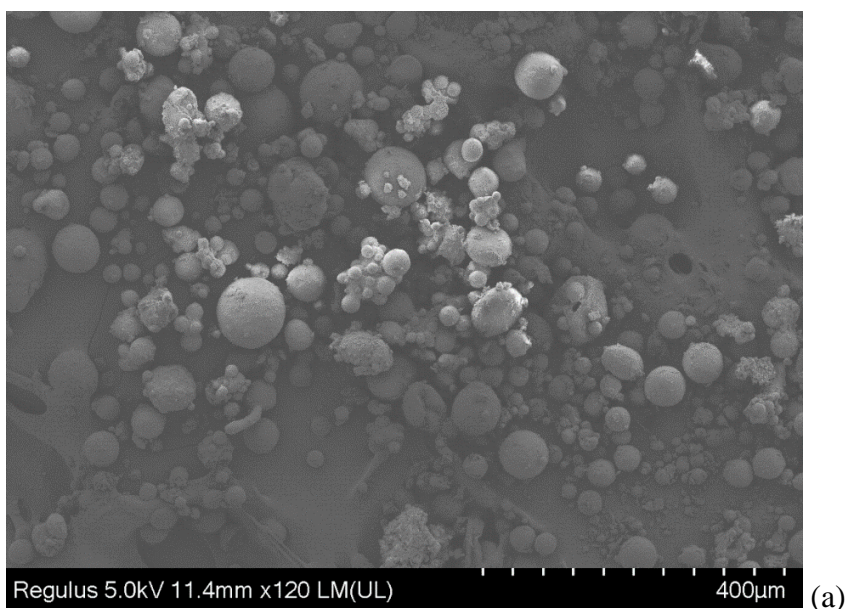
Figure 4.2. SEM images of particle morphology of poly (AN/MMA )(50/50 mol %) microspheres. Zoom-in images (a: scale bar =100µm, b: scale bar =100µm (with particle diameters), c: scale bar =40µm)

The oil phase system is composed of MMA, AN and blowing agent; however, only AN and MMA participate in the polymerization. The particle droplets with core-shell interface, where the shell layer is formed by polymer solution, will be visible. The resulting polymers will precipitate in the oil phase and migrate to the surface due to phase separation. The blowing agent

will diffuse to the core of the droplet. As the polymerization reaction proceeds, secondary particles will be formed on the surface of the microspheres as a result of the water phase polymerization of AN.

Solubility of AN in water is responsible for this secondary nucleation when AIBN is used as an initiator. At 20°C, the solubility of acrylonitrile in water is 7.35%, whereas the solubility of methyl methacrylate in water is only 1.59% (Min & Ray, 1974). Since AIBN is considered to be an oil soluble initiator, the presence of AN and MMA in water will increase the water solubility of AIBN (Zhang & Ray, 1997; Lu et al., 2006). Therefore, polymerization of AN in water will be triggered with the AIBN initiator, and the AN content in the oil phase will be decreased due to the migration of AN monomer from the oil phase to the water phase. When the polymerization further progresses, the shell layer continues to increase its thickness, and the diffusion of the blowing agent to the center of the droplets continues. Eventually, core-shell microspheres are formed with the blowing agent as the core, and the resulting polymer comprises the shell. The secondary particles generated from the water phase polymerization will be adsorbed on the surface of the microspheres.

The morphology of AN and MMA copolymer microspheres when AN was 60 mol % substituted by MMA is showed in Figure 4.3. Secondary particles on the surface of the microspheres are also observed from the SEM images.



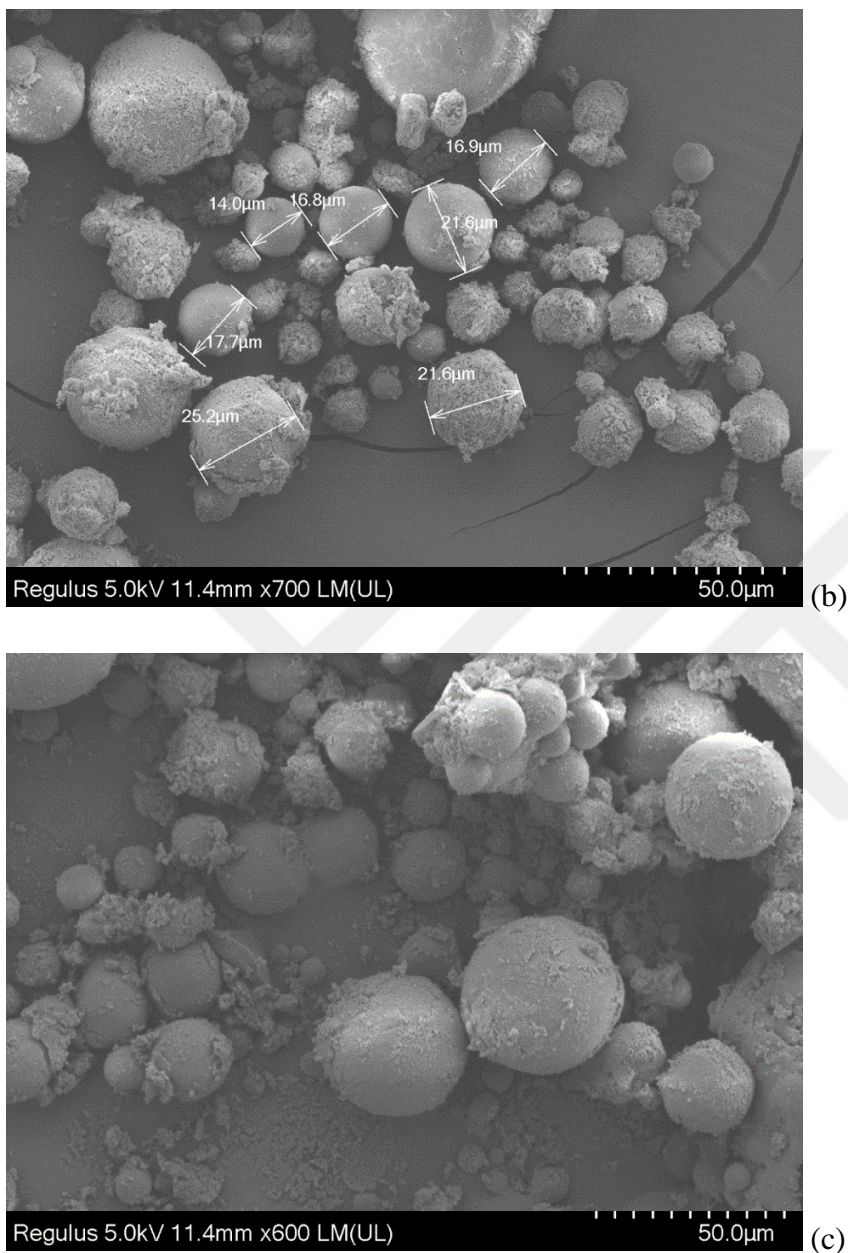
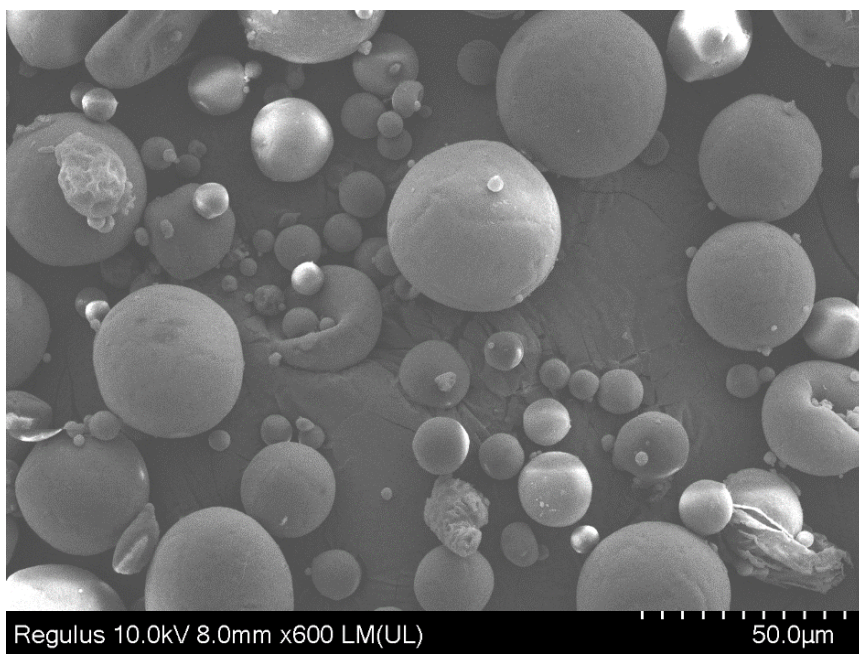
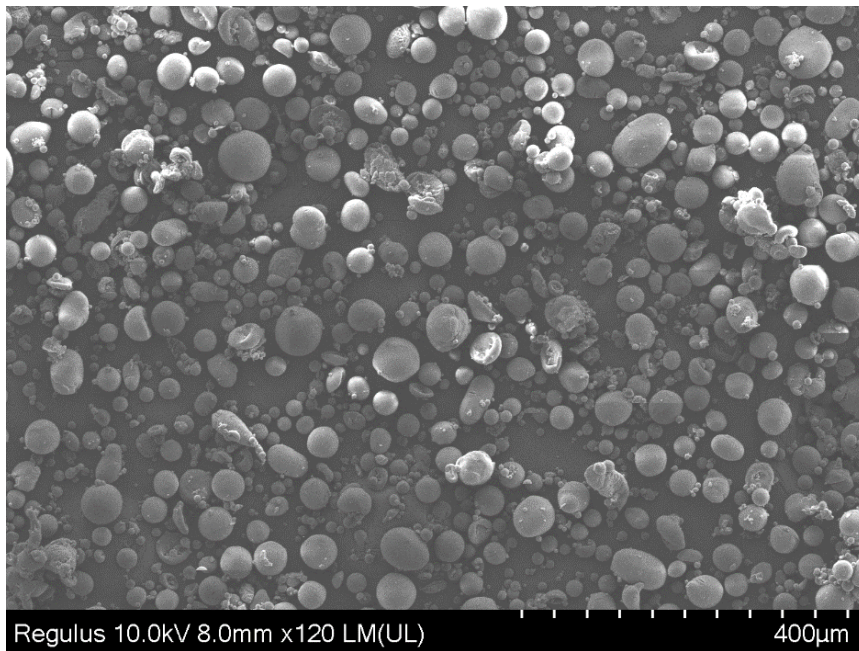


Figure 4.3. SEM images of particle morphology of poly (AN/MMA)(40/60 mol %) microspheres. Zoom-in images (a: scale bar =400μm, b: scale bar =50μm (with particle diameters), c: scale bar =50μm)

When lauryl peroxide is used as initiator with a monomer ratio AN/MMA (65/35 mol %), the morphology shows that microspheres are formed with smooth surface and there are no

trace of secondary particles (Figure 4.4). This implies that LPO cannot initiate the water phase polymerization to produce secondary particles.



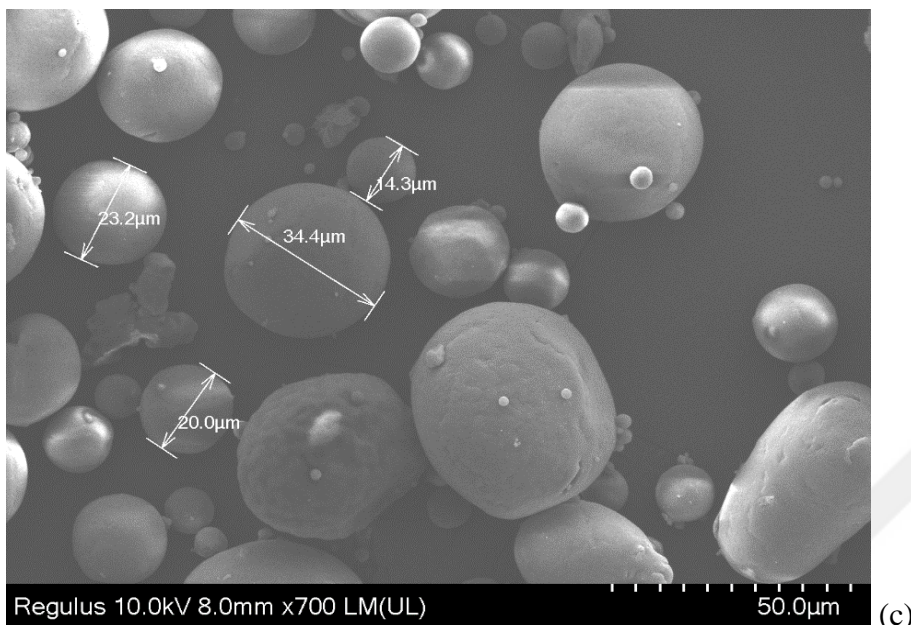


Figure 4.4. SEM images of particle morphology of poly (AN/MMA) (65/35 mol %) microspheres. Zoom-in images (a: scale bar =400 $\mu$ m, b: scale bar =50 $\mu$ m (with particle diameters), c: scale bar =50 $\mu$ m)

#### 4.2 Effect of the blowing agent

The thermogravimetric analysis curve (Figure 4.5) shows the blowing agent content of microspheres prepared with different blowing agents and different initiators. Two-step decomposition was observed from the TGA curves. In the first stage, eruption and evaporation of the blowing agent occurred, followed by the decomposition of the polymeric shell in the second stage. Heating upon the microspheres above the boiling point of the blowing agent, the gasified hydrocarbon pressure will initiate the expansion and try to burst the polymer shell. Consequently, the microspheres begin to lose their weight above the boiling point of the hydrocarbon. The penetration of the gasified hydrocarbon by the shell depends on the gas permeability property of the shell-forming polymer. The large blowing agent contents in figure 4.5 proves the excellent gas barrier property of Polyacrylonitrile (PAN) (Allen et al., 1977). When polymerization is carried out at 60°C with a hydrocarbon mixer of n-pentane and isopentane (ratio 1:1), the first decomposition temperature is 95°C, and the volatile content is

about 4.45%. The decomposition temperature increased when n-hexane, heptane and n-octane were used as blowing agents. When n-hexane was used as a blowing agent, 21.43% blowing agent was captured as core material, and the first decomposition temperature was 150°C. When mixed core materials were used, the blowing agent content also changed. The amount of blowing agents encapsulated on the microspheres prepared with a mixer of n-hexane and heptane (1:1 ratio), and n-hexane and n-octane (1:1) were 17.03% and 29.70%, respectively.

Figure 4.2(a) shows that microspheres become porous, with holes deformity on the surface when n-pentane and isopentane were used as core materials. If the boiling point of the blowing agent is lower than the polymerization temperature, then there will be a high blowing agent concentration in the gas phase resulting in a higher monomer concentration and a lower blowing agent concentration in the oil phase. As the reaction progresses, precipitation of the resulting polymer chain becomes slower, and phase separation occurs in the oil phase.

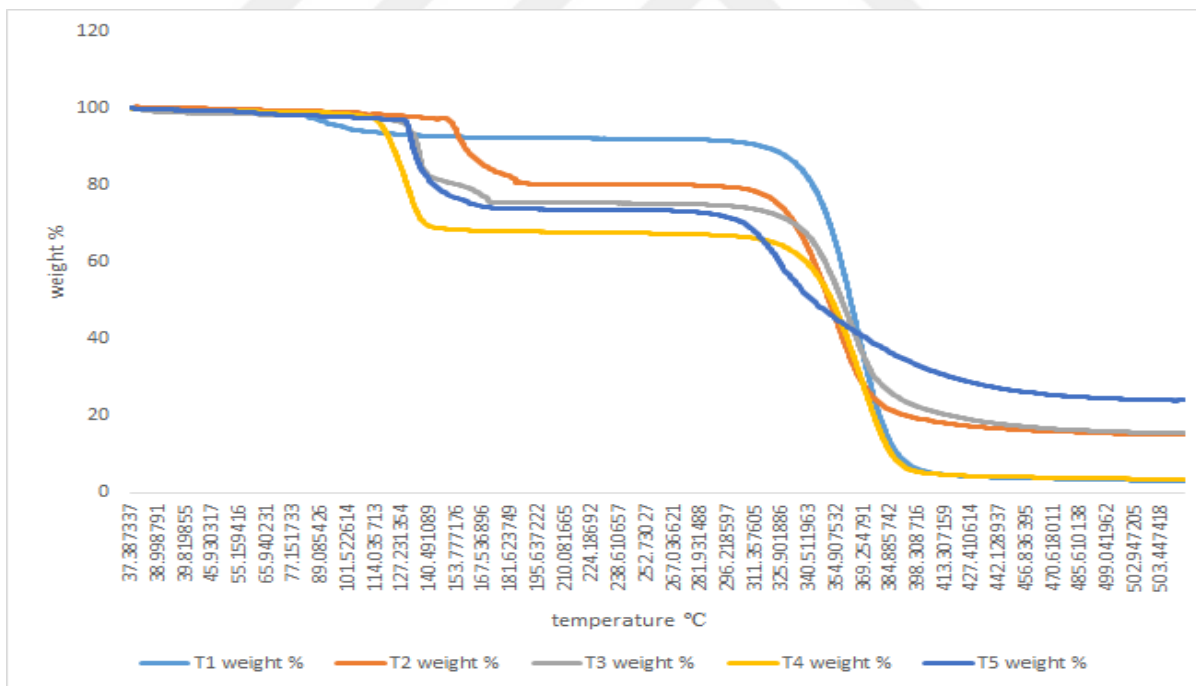


Figure 4.5 Thermogravimetric analysis curves of microspheres prepared with different blowing agents

Therefore, microspheres with n-pentane and isopentane as blowing agents have a porous and deformed structure as the boiling point of n-pentane and isopentane are 36.1 and 27.8°C,

respectively. The boiling point of n-hexane, heptane, and n-octane is 68.7, 98.42, and 125.6°C, respectively, which are higher than the polymerization temperature. Consequently, the core-shell structure is formed as the resulting polymer is quickly and fully separated from the oil phase (Figure 4.3, Figure 4.4).

### 4.3 Structural characterization of the microspheres

Figure 4.6 shows the infrared spectra of the thermally expandable microsphere prepared with AN and MMA as the monomer and n-pentane and isopentane as blowing agents. It can be seen from the spectrum that a sharp absorption peak is located at around  $2241\text{ cm}^{-1}$ , which is the characteristic absorption peak of  $\text{-C}\equiv\text{N}$  (nitrile stretching) belongs to the monomer AN. The sharp absorption peak at  $1731\text{ cm}^{-1}$  is a peak of  $\text{-C=O}$  (carbonyl peak) stretching vibration which belongs to MMA monomer (Gupta et al., 2016). Furthermore the characteristic absorption peak at  $\sim 2950\text{-}2990\text{ cm}^{-1}$  corresponds to  $\text{-C-H}$  stretching in saturated hydrocarbon namely alkane.

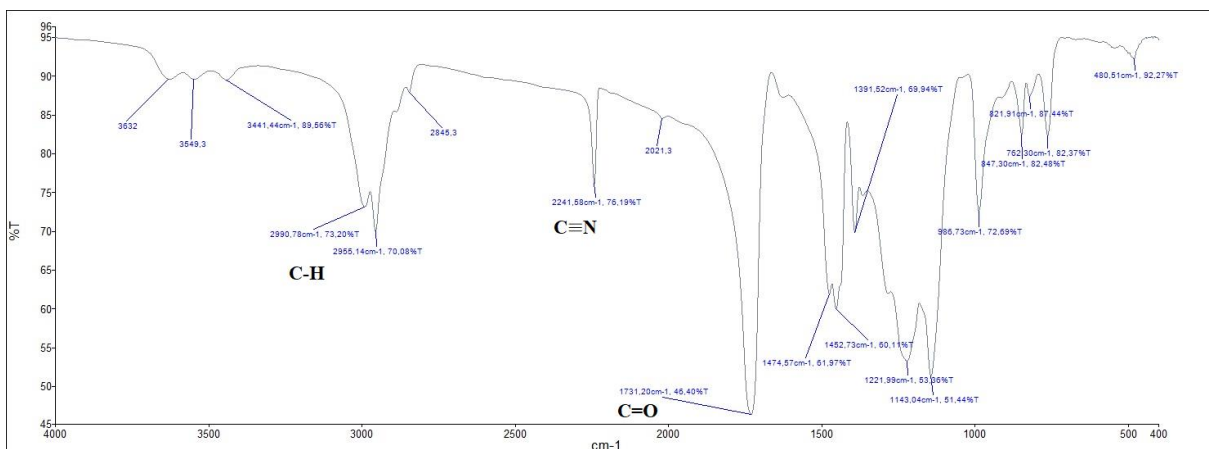


Figure 4.6 FTIR spectra of the thermally expandable microsphere with poly-(AN-MMA) copolymer shell and n-pentane+isopentane mixture as the core material

#### 4.4 Influence of initiators

Figure 4.7 shows that when AIBN was used as initiator, the surface of the microspheres covered with many secondary particles. Contrarily, when LPO was used as initiator, particles were formed with a smooth surface without secondary particles (Figure 4.4 (b)). As mentioned earlier, monomers such as AN, which has low solubility in water, would trigger the polymerization of AN in the continuous phase with AIBN initiator whereas LPO cannot initiate the water phase polymerization of AN (Ma et al., 2004).

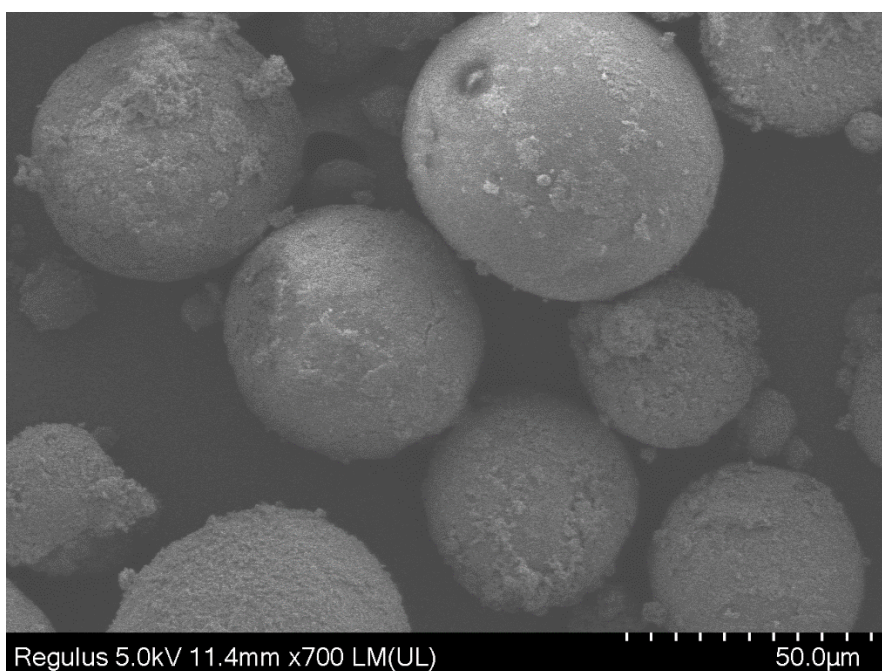
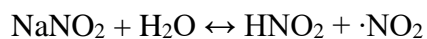
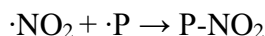
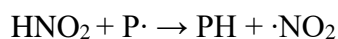


Figure 4.7 Morphology of microspheres prepared with AIBN initiator in absence of inhibitor ( $\text{NaNO}_2$ )

Figure 4.8 shows that when inhibitor like  $\text{NaNO}_2$  was introduced along with AIBN, microspheres become very smooth and round, effectively preventing secondary nucleation. Water phase polymerization is inhibited with the presence of  $\text{NaNO}_2$  which captures the free radicals in the water phase.  $\text{NaNO}_2$  effectively prevented the formation of the secondary particles and the inhibition mechanism of  $\text{NaNO}_2$  is shown as follows:





where P represents growing oligoradical (Ma et al., 2001).

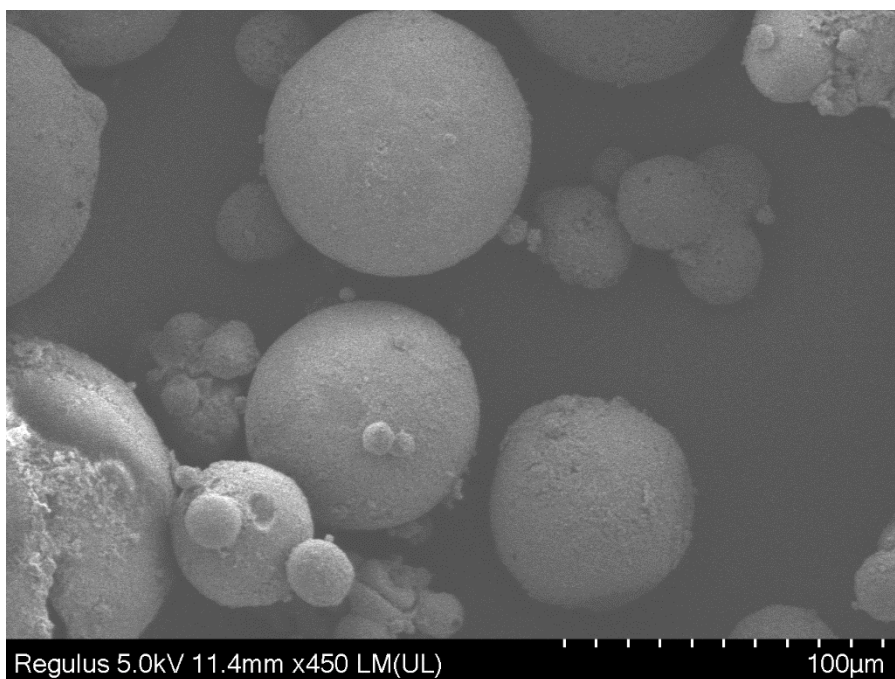


Figure 4.8 Morphology of microspheres when  $\text{NaNO}_2$  is added along with AIBN initiator

#### 4.5 Thermal property of the particle shell

Figure 4.9 shows the DTA analysis of the thermally expandable microspheres with different monomer compositions and blowing agent types. Figure 4.9(a) shows that microspheres began to absorb heat from  $90^\circ\text{C}$  and exhibited a prominent endothermic peak at  $96^\circ\text{C}$ . This outcome indicates that the onset temperature of sample T-1 was  $90^\circ\text{C}$ . At this temperature, only a tiny portion of microspheres expanded. Most microspheres absorb heat at the peak temperature ( $96^\circ\text{C}$ ) and expand extensively. The peak temperatures along with the expansion enthalpy are all listed in Table 4.2. The expansion enthalpy of the microspheres ( $\Delta H$ ) represents the energy absorbed by the microspheres during their expansion (Fu et al., 2019). The polymeric chains of the microsphere shell use this energy to activate their motion. Microspheres

also use this energy to gasify the blowing agents (alkanes). The sharp and narrow endothermic peak in DTA curves of sample T-4 shows that most of the microspheres expand at 133.88°C (Figure 4.9(d)). From figure 4.10, it is evident that the expansion enthalpy ( $\Delta H$ ) increased from sample T-1 to T-5 with a much sharper and narrower absorption peak. This difference among the absorption peaks may be due to the irregularity of the polymer shell thickness. For microspheres with regular and spherical shell structures, the internal pressure exerted by the gasified core material will be uniform, and we will find a narrow expansion temperature range.

Table 4.2 DTA parameters of microspheres with different monomer ratio and blowing agents

Entry (Sample code)	Peak temperature (°C)	Enthalpy change, $\Delta H$ (J/g)
2 (T1)	96.85	29.3718
8 (T2)	160.32	33.6251
10 (T3)	139.29	39.3810
11 (T4)	133.88	88.7526
12 (T5)	137.54	61.2351

Combining thermogravimetric analysis with the expansion enthalpy of the microspheres, we can conclude that the increase in the enthalpy of expansion was due to the rise in the blowing agent contents. Microspheres will need a higher amount of energy to gasify their larger amount of blowing agents and activate the motion of the polymeric chains in the shell.

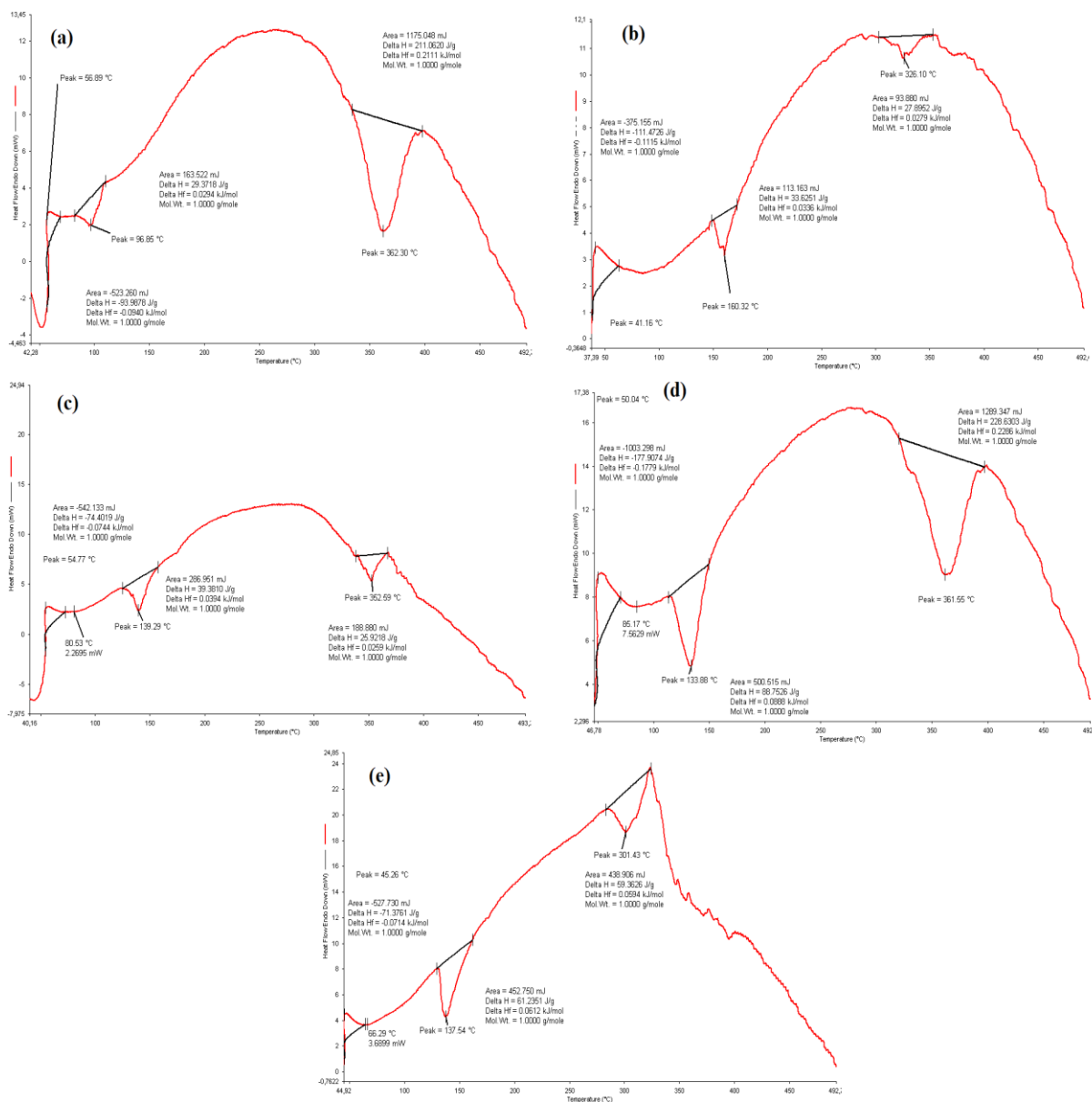


Figure 4.9 DTA curves of microspheres with different monomer ratio and blowing agent type (a: sample c: T1, b: sample T2, c: sample T3, d: sample T4, e: sample T5)

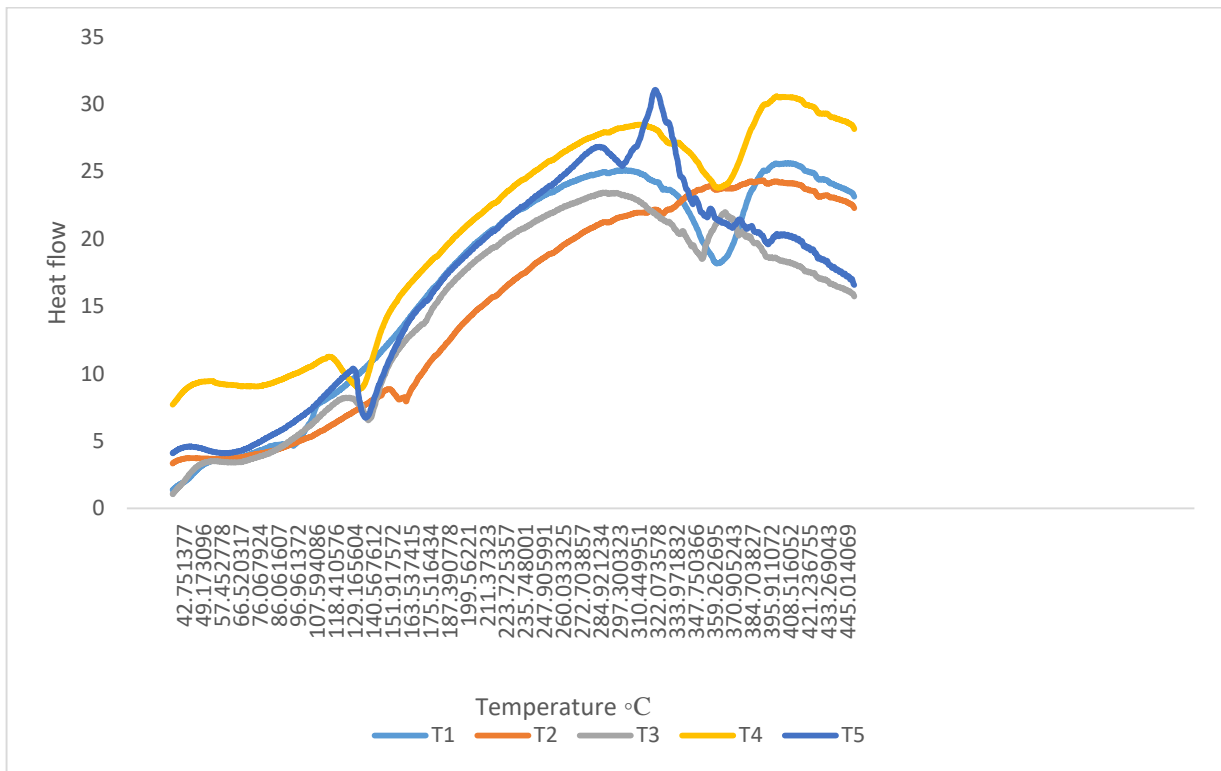


Figure 4.10 Comparison of DTA data of thermally expandable microspheres T1-T5

#### 4. CONCLUSION AND RECOMMENDATIONS

In the present study, thermally expandable microspheres with core-shell structure (Figure 5.1) were prepared by suspension polymerization, where we optimized the process to conduct it under atmospheric pressure. When only AN was used as the monomer (100 mol%), we could not obtain TEMs. However, the presence of 65% to 40% AN and 35% to 60% MMA enabled us to get TEMs. When a 40:60 ratio of AN: MMA was used with a mixture of n-hexane and n-octane (ratio 1:1) as core material, we found the highest yield of TEMs with a 29.7% blowing agent content. Figure 5.2 shows that the volume of the microspheres was increased about 3.5 times the actual volume using the same AN to MMA weight ratio at 105°C.  $\text{NaNO}_2$  inhibitor was used along with AIBN initiator to prevent water phase polymerization, resulting in the formation of secondary particles on the surface of the TEMs. In contrast, LPO did not trigger the secondary nucleation and produced particles with smooth and round structures. The thermal properties of the TEMs vary upon the monomer composition and blowing agent type.

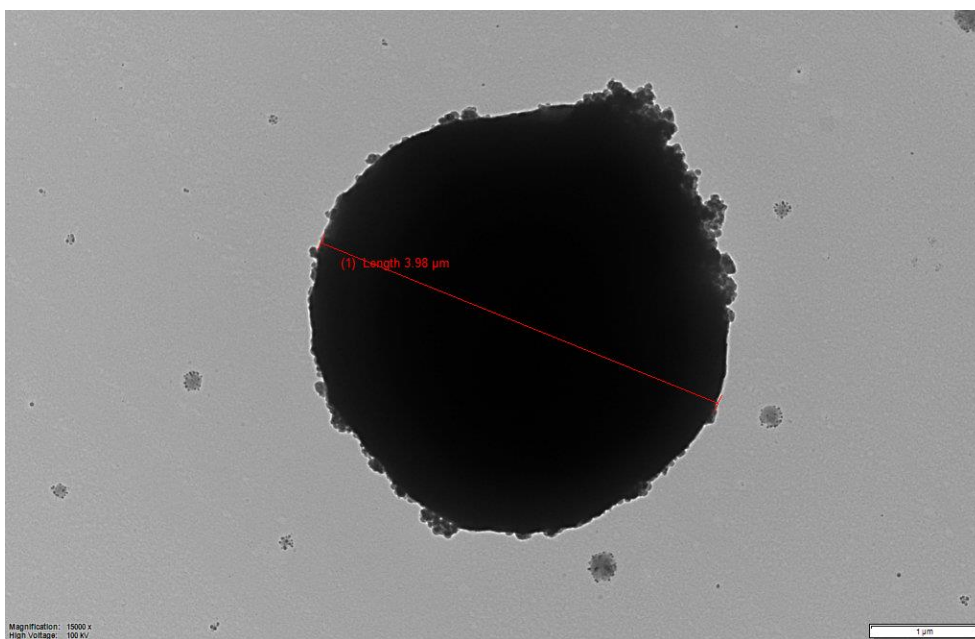


Figure 5.1 TEM analysis of thermally expandable microspheres (Sample T-1, Table 1)

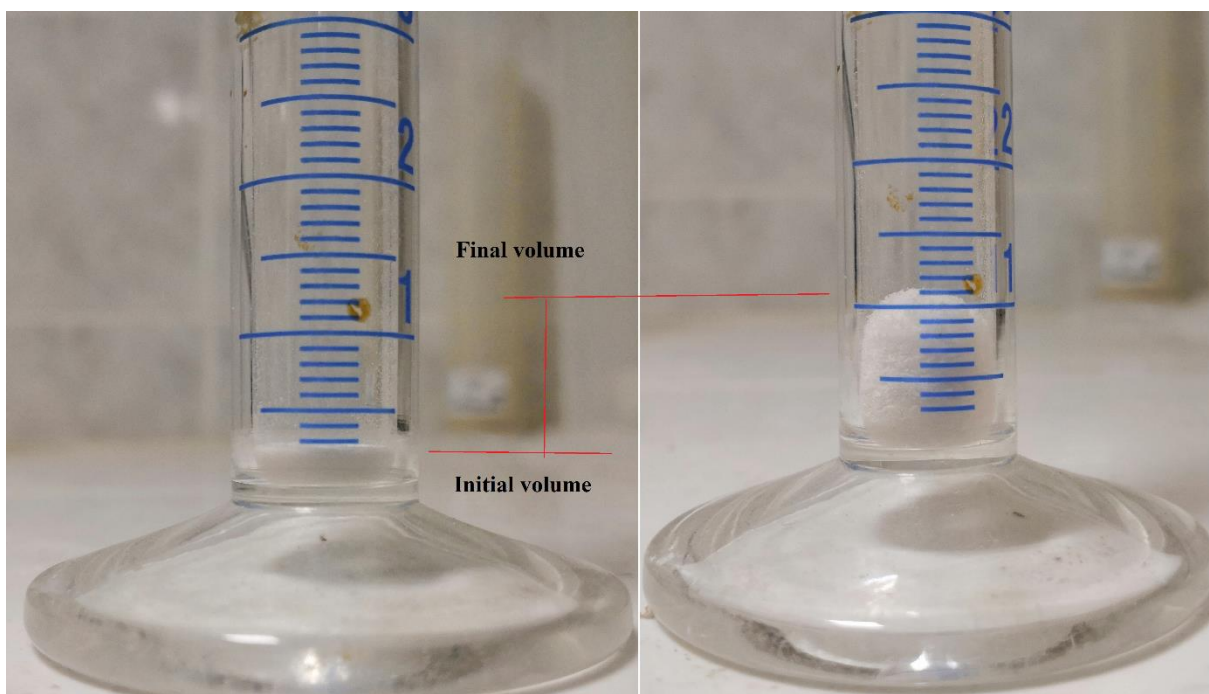


Figure 5.2 Digital photographs of (a) unexpanded microspheres and (b) expanded microspheres (90-105°C)

## REFERENCES

- Allen, S. M., Fujii, M., Stannett, V., Hopfenberg, H. B., & Williams, J. L. (1977). The barrier properties of polyacrylonitrile. *Journal of Membrane Science*, 2, 153-163.
- Arshady, R. (1992). Suspension, emulsion, and dispersion polymerization: A methodological survey. *Colloid and polymer science*, 270(8), 717-732.
- Arshady, R. (Ed.). (1999). *Microspheres Microcapsules & Liposomes: Medical & biotechnology applications*. Citus Books.
- Bals, E., Breedt, J., Spiteri, W. L., & Goosen, A. J., (1996). Porous prilled ammonium nitrate. *U.S. Patent No. 5,540,793*. Washington, DC: U.S. Patent and Trademark Office..
- Benita, S. (Ed.). (2005). *Microencapsulation: methods and industrial applications*. Crc Press.
- Burgess, D. J., & Carless, J. E. (1985). Manufacture of gelatin/gelatin coacervate microcapsules. *International journal of pharmaceutics*, 27(1), 61-70.
- Cocker, T. M., Fee, C. J., & Evans, R. A. (1997). Preparation of magnetically susceptible polyacrylamide/magnetite beads for use in magnetically stabilized fluidized bed chromatography. *Biotechnology and bioengineering*, 53(1), 79-87.
- Deveci, S. S., & Basal, G. (2009). Preparation of PCM microcapsules by complex coacervation of silk fibroin and chitosan. *Colloid and polymer science*, 287(12), 1455-1467.
- Ebewele, R. O. (2000). *Polymer science and technology*. CRC press.
- Erdem, B., Sudol, E. D., Dimonie, V. L., & El-Aasser, M. S. (2000). Encapsulation of inorganic particles via miniemulsion polymerization. I. Dispersion of titanium dioxide particles in organic media using OLOA 370 as stabilizer. *Journal of Polymer Science Part A: Polymer Chemistry*, 38(24), 4419-4450.
- Fredlund, J. (2011). Synthesis of Thermo Expandable Microspheres.

**REFERENCES (continued)**

- Fried, J. R. (2014). *Polymer science and technology*. Pearson Education.
- Fu, H., Gong, W., Chen, B., Chen, Y., Ban, D., Yin, X., ... & He, L. (2019). Influence of electrolytes on thermal expansion microcapsules. *Journal of Macromolecular Science, Part A*, 56(1), 104-114 .
- Gottlob, K. (1915) U.S. Patent No. 1,149,577.
- Gouin, S. (2004). Microencapsulation: industrial appraisal of existing technologies and trends. *Trends in food science & technology*, 15(7-8), 330-347.
- Gupta, N., Rai, R., Sikder, A., Nandi, S., Tanwar, A., Khatokar, R., ... & Mitra, S. (2016). Design and development of a poly (acrylonitrile-co-methyl methacrylate) copolymer to improve the viscoelastic and surface properties critical to scratch resistance. *RSC advances*, 6(44), 37933-37937.
- Hofman, F., Delbruck, K. (1909) German Patent No. 250 690.
- Horák, D., Boháček, J., & Šubrt, M. (2000). Magnetic poly (2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) microspheres by dispersion polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, 38(7), 1161-1171.
- Hou, Z., Xia, Y., Qu, W., & Kan, C. (2015). Preparation and properties of thermoplastic expandable microspheres with P (VDC-AN-MMA) shell by suspension polymerization. *International Journal of Polymeric Materials and Polymeric Biomaterials*, 64(8), 427-431.
- Huang, M. R., Li, X. G., Li, S. X., & Zhang, W. (2004). Resultful synthesis of polyvinyltetrazole from polyacrylonitrile. *Reactive and Functional Polymers*, 59(1), 53-61.
- Huang, Y. (2004). *Preparation of thermally expandable polymer particles*. Lehigh University.

**REFERENCES (continued)**

- Jalili, K., Abbasi, F., Nasiri, M., Ghasemi, M., & Haddadi, E. (2009). Preparation and characterization of expandable St/MMA copolymers produced by suspension polymerization. *Journal of cellular plastics*, 45(3), 197-224.
- Jonsson, M. (2010). *Thermally Expandable Microspheres Prepared via Suspension Polymerization-Synthesis, Characterization, and Application* (Doctoral dissertation, KTH).
- Jonsson, M., Nordin, O., Malmström, E., & Hammer, C. (2006). Suspension polymerization of thermally expandable core/shell particles. *Polymer*, 47(10), 3315-3324.
- Jonsson, M., Nordin, O., Kron, A. L., & Malmström, E. (2010). Influence of crosslinking on the characteristics of thermally expandable microspheres expanding at high temperature. *Journal of applied polymer science*, 118(2), 1219-1229.
- Kondo, A., Kamura, H., & Higashitani, K. (1994). Development and application of thermo-sensitive magnetic immunomicrospheres for antibody purification. *Applied microbiology and biotechnology*, 41(1), 99-105.
- Kydonieus, A.F. (Ed.). (1980). *Controlled Release Technologies: Methods, Theory, and Applications: Methods, Theory, and Applications* (1st ed.). CRC Press.
- Lee, Y., Rho, J., & Jung, B. (2003). Preparation of magnetic ion-exchange resins by the suspension polymerization of styrene with magnetite. *Journal of applied polymer science*, 89(8), 2058-2067.
- Lu, Q., Weng, Z. X., Shan, G. R., Lai, G. Q., & Pan, Z. R. (2006). Effect of acrylonitrile water solubility on the suspension copolymerization of acrylonitrile and styrene. *Journal of applied polymer science*, 101(6), 4270-4274.
- Ma, G. H., Nagai, M., & Omi, S. (2001). Study on preparation of monodispersed poly (styrene-co-N-dimethylaminoethyl methacrylate) composite microspheres by SPG (Shirasu Porous Glass) emulsification technique. *Journal of applied polymer science*, 79(13), 2408-2424.

**REFERENCES (continued)**

- Ma GH, Sone H, Omi S (2004) Preparation of uniform-sized polystyrene- polyacrylamide composite microspheres from a W/O/W emulsion by membrane emulsification technique and subsequent suspension polymerization. *Macromolecules* 37:2954-2964.
- Min, K. W., & Ray, W. H. (1974). On the mathematical modeling of emulsion polymerization reactors.
- Nelson, G. (2013). Microencapsulated colourants for technical textile application. In *Advances in the Dyeing and Finishing of Technical Textiles* (pp. 78-104). Woodhead Publishing.
- Nimmannit, U., & Suwanpatra, N. (1996). Microencapsulation of drugs by the coacervation technique using ethylcellulose and acrylate-methacrylate copolymer as wall materials. *Journal of microencapsulation*, 13(6), 643-649.
- Rheem, M. J., Jung, H., Ha, J., Baeck, S. H., & Shim, S. E. (2017). Suspension polymerization of thermally expandable microspheres using low-temperature initiators. *Colloid and Polymer Science*, 295(1), 171-180.
- Senna, M., & Lee, J. (1995). Preparation of monodispersed polystyrene microspheres uniformly coated by magnetite via heterogeneous polymerization. *Colloid and Polymer Science*, 273(1), 76-82.
- Soane, D. S., & Houston, M. R. (2003). *U.S. Patent No. 6,617,364*. Washington, DC: U.S. Patent and Trademark Office.
- Silvério Neto, W., Thyago Jensen, A., Ribeiro Ferreira, G., Fonseca Valadares, L., Gambetta, R., Belém Gonçalves, S., & Machado, F. (2015). A survey on synthesis processes of structured materials for biomedical applications: Iron-based magnetic nanoparticles, polymeric materials and polymerization processes. *Current pharmaceutical design*, 21(37), 5336-5358.
- Ugelstad, J., Berge, A., Ellingsen, T., Schmid, R., Nilsen, T. N., Mørk, P. C., ... & Olsvik, Ø. (1992). Preparation and application of new monosized polymer particles. *Progress in Polymer Science*, 17(1), 87-161.

**REFERENCES (continued)**

- Vivaldo-Lima, E., Wood, P. E., Hamielec, A. E., & Penlidis, A. (1997). An updated review on suspension polymerization. *Industrial & engineering chemistry research*, 36(4), 939-965.
- Wedlock, D. J. (2012). *Controlled particle, droplet and bubble formation*. Butterworth-Heinemann.
- Yanase, N., Noguchi, H., Asakura, H., & Suzuta, T. (1993). Preparation of magnetic latex particles by emulsion polymerization of styrene in the presence of a ferrofluid. *Journal of applied polymer science*, 50(5), 765-776.
- Yang, C., Liu, H., Guan, Y., Xing, J., Liu, J., & Shan, G. (2005). Preparation of magnetic poly (methylmethacrylate–divinylbenzene–glycidylmethacrylate) microspheres by spraying suspension polymerization and their use for protein adsorption. *Journal of Magnetism and Magnetic Materials*, 293(1), 187-192.
- Yi, Q., Li, J., Zhang, R., Ma, E., & Liu, R. (2021). Preparation of small particle diameter thermally expandable microspheres under atmospheric pressure for potential utilization in wood. *Journal of Applied Polymer Science*, 138(4), 49734.
- Yokomizo T, Tanaka K, Niinuma K. JP 9019635; 1997.
- Yuan, H. G., Kalfas, G., & Ray, W. H. (1991). Suspension polymerization. *Journal of Macromolecular Science, Part C: Polymer Reviews*, 31(2-3), 215-299.
- Zhang, S. X., & Ray, W. H. (1997). Modeling and experimental studies of aqueous suspension polymerization processes. 3. Mass-transfer and monomer solubility effects. *Industrial & engineering chemistry research*, 36(4), 1310-1321.
- Zhou, S., Zhou, Z., Ji, C., Xu, W., Ma, H., Ren, F., & Wang, X. (2017). Formation mechanism of thermally expandable microspheres of PMMA encapsulating NaHCO<sub>3</sub> and ethanol via thermally induced phase separation. *RSC advances*, 7(80), 50603-50609.
- Zygmunt, B., & Buczkowski, D. (2007). Influence of ammonium nitrate pills' properties on detonation velocity of ANFO. *Propellants, Explosives, Pyrotechnics: An International Journal Dealing with Scientific and Technological Aspects of Energetic Materials*, 32(5), 411-414.