ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PREPARATION OF STYRENATED OIL BY CONTROLLED/LIVING RADICAL POLYMERIZATION IN MINIEMULSION

Ph.D. THESIS

Mesut YILMAZOĞLU

Department of Chemical Engineering

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JANUARY 2017

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MİNİEMÜLSİYON KOŞULLARINDA KONTROLLÜ/YAŞAYAN RADİKAL POLİMERİZAYONUYLA STİRENLENMİŞ YAĞLARIN HAZIRLANMASI

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Mesut YILMAZOĞLU, **a Ph.D.** student of İTU Graduate School of Science Engineering and Technology student ID **506102010**, successfully defended the **thesis/dissertation** entitled **"PREPARATION OF STYRENATED OIL BY CONTROLLED/LIVING RADICAL POLYMERIZATION IN MINIEMULSION"**, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my lovely family,

FOREWORD

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ABBREVIATIONS

ABLO : Air blown linseed oil
AIBN : 2,2 Azobis (isobutyronitrile)
ATRP : Atom transfer radical polymerization
RAFT : Reversible addition-fragmentation chain transfer polymerization
NMRP : Nitroxide mediated radical polymerization
ACPC : 4,4'-azobis-4-cyanopentanoyl chloride
ACPA : 4,4'-azobis-4-cyanopentanoic acid
PMDC : Phenacyl morpholine dithiocarbamate
CTAB : Cetyl trimethyl ammonium bromide
HD : Hexadecane
PG : Partial gliceryde
PDI : Polydispersity index
TEMPO : 2,2',6,6'-tetramethylpiperidinyl-1-oxy
FT-IR : Fourier-Transform infrared spectrum
DLS : Dynamic light scattering
GPC : Gel permeation chromotography

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PREPARATION OF STYRENATED OIL BY CONTROLLED/LIVING RADICAL POLYMERIZATION IN MINIEMULSION

SUMMARY

In the first part of the thesis, styrenated oil products were prepared in miniemulsion conditions by reversible addition-fragmentation chain transfer polymerization (RAFT) technique using phenacyl morpholine dithiocarbamate (PMDC) as a RAFT agent. First, hydroperoxide groups were formed on the oil structure by air-blowing process. Then the prepared miniemulsion of styrene-air blown linseed oil (ABLO) was subjected to styrenation in the presence of the RAFT agent. Miniemulsion was prepared by means of ultrasonication by using cetyl trimethyl ammonium bromide (CTAB) and hexadecane (HD) as surfactant and co-surfactant, respectively. Ideal miniemulsion condition was determined by following the change of droplet/particle sizes during the reactions carried out at different surfactant concentrations. The styrenated oil product obtained under optimum conditions was characterized by FT-IR, ^{1}H-NMR and GPC measurements. In order to understand the effect of miniemulsion conditions on molecular weight and polydispersity index (PDI), styrenated oil samples were also prepared in solvent (dioxane) medium for the purpose of comparison. Tests for film properties of product prepared by RAFT in miniemulsion medium were applied according to related standards. The styrenated oil obtained in this way exhibit molecular weight distribution values (1.71 and 1.76 for 24 h and 48 h, respectively) which are lower than styrenated oil products obtained by the classical RAFT polymerization in solvent medium. The film properties showed that these styrenated oil samples could be used as an oil based binder.

In the second part of the thesis, triglyceride oil-styrene copolymerization was carried out with nitroxide mediated radical polymerization (NMRP) technique in miniemulsion. For this purpose, firstly, 4,4'-azobis-4-cyanopentanoyl chloride (ACPC) was synthesized from 4,4'-azobis-4-cyanopentanoic acid (ACPA). Macroazoinitiator, which comprises thermally labile azo groups, was obtained with reaction of partial glicerydes (PGs) of linseed oil and ACPC. Then, oil-based macroazoinitiator and styrene mixture was subjected to styrenation in the presence of nitroxide radical 2,2',6,6'-tetramethylpiperidinyl-1-oxy (TEMPO) in order to obtain styrenated oil product with low PDI and good film properties in miniemulsion medium. Miniemulsion mixture was prepared by ultrasonication process by using DOWFAX 8390 and HD as surfactant and costabilizer, respectively. Miniemulsion polymerization was carried out at different surfactant concentrations in order to determine the appropriate surfactant concentration. Droplet and particle sizes were followed throughout the reaction in each process. Products obtained by ideal process were characterized by FT-IR, ^{1}H-NMR and GPC measurements. Styrenation process was also performed by solution polymerization in xylene to understand the effect of miniemulsion medium. Film properties of oil samples were evaluated according to related standards. As a result, styrenation process could be successfully carried out

with NMRP adapted miniemulsion polymerization preserving colloidal stability and samples obtained in this process showed low PDI values and good film properties.

MİNİEMÜLSİYON KOŞULLARINDA KONTROLLÜ/YAŞAYAN RADİKAL POLİMERİZAYONUYLA STİRENLENMİŞ YAĞLARIN HAZIRLANMASI

ÖZET

Trigliserid yağlar, yüzey kaplama malzemeleri üretiminde ve boya endüstrisinde kullanılan organik malzemelerdir. Yüzey kaplama malzemesi olarak yeterli ve olumlu film özellikleri gösteremediklerinden yağların çeşitli modifikasyonlara uğratılması ve özelliklerinin iyileştirilmesi gereklidir. Vinil monomerleri ile olan kopolimer ürünleri de bu modifikasyonlarla oluşturulan ve iyi film özellikleri gösteren malzemelerdir. Bu amaçla gerçekleştirilen kopolimerizasyon proseslerinde en çok kullanılan vinil monomeri stirendir. Yağların stiren ile kopolimerizasyonunda karşılaşılan en büyük problem ise homopolistiren oluşumudur. Stirenlenmiş yağların çabuk kuruma, düşük asit değeri, pigmentlerle kararlı bileşik oluşturma, suya dayanıklılık gibi birçok üstünlüğüne rağmen söz konusu stirenleme işlemlerinde karşılaşılan homopolistiren oluşumu film özelliklerini olumsuz etkilemekte, kaplamalarda bulanıklığa yol açmaktadır. Film özellikleri üzerinde olumsuz etkileri nedeniyle bu proseslerde homopolistiren oluşumunun önlenmesi gerekir.

Bu tez çalışmasında keten yağı/stiren kopolimerizasyonu kontrollü/yaşayan radikal polimerizasyonu yöntemlerinden RAFT ve NMRP teknikleri ile miniemülsiyon koşullarında gerçekleştirilmiştir. Çalışma sonucunda, miniemülsiyon koşullarında elde edilen keten yağı/stiren kopolimer ürünlerinin molekül ağırlığı dağılımlarının çözücü ortamında kontrollü polimerizasyonla elde edilen ürünlere göre düşük olduğu ve kaplama malzemesi olarak kullanılmaya uygun film özellikleri gösterdikleri görülmüştür.

Tez çalışmasının ilk kısmında RAFT ajanı varlığında miniemülsiyon koşullarında hava üflenmiş keten yağının stirenlenme prosesi gerçekleştirilmiştir. Bu çalışmada, stirenlenmiş yağ ürünleri, RAFT ajanı olarak fenasil morfolin ditiyokarbamat (PMDC) kullanılarak miniemülsiyon koşulları altında hazırlanmıştır. İlk olarak, hava üfleme prosesi ile yağ yapısında hidroperoksit grupları oluşturulmuş, stiren ve hava üflenmiş yağdan oluşan karışım RAFT ajanı varlığında ultrasonikasyon işlemiyle miniemülsiyona dönüştürülmüştür. Miniemülsiyon polimerizasyonunda sırasıyla surfaktan ve kosurfaktan olarak setil trimetil amonyum bromür (CTAB) ve hekzadekan (HD) kullanılmıştır. İdeal miniemülsiyon koşulları, farklı surfaktan konsantrasyonlarında gerçekleştirilen denemelerde reaksiyon boyunca damlacık/partikül boyutunun değişmemesi esasına dayanan bir strateji ile DLS analizleri değerlendirilerek belirlenmiştir. Bu şekilde, damlacıklar arasındaki monomer difüzyonunun ortadan kaldırılması için uygun koşullar oluşturulmuştur. Optimum koşullar altında elde edilen stirenlenmiş yağ ürünleri FT-IR, ^{1}H-NMR ve GPC ölçümleri ile karakterize edilmiştir. Miniemülsiyon koşullarının molekül ağırlığı ve polidispersite indeksi (PDI) üzerindeki etkisini anlamak için, çözücü (dioksan) ortamında stirenlenmiş yağ örnekleri de hazırlanmıştır. Bu çalışmada elde edilen stirenlenmiş yağ ürünleri, çözücü ortamında klasik RAFT polimerizasyonu ile

elde edilen stirenlenmiş yağ ürünlerinden daha düşük molekül ağırlığı dağılım değerleri sergilemiştir. Film testleri, stirenlenmiş yağ örneklerinin yağ bazlı kaplama malzemesi olarak kullanılabileceğini göstermiştir.

Tez çalışmasının ikinci kısmında trigliserid yağların miniemülsiyon polimerizasyonuyla stirenleme prosesi; a) keten yağından kısmi gliseridlerin elde edilmesi, b) kısmi gliseridlerin azo grubu içeren ACPC ile reaksiyona sokularak makroazobaşlatıcının elde edilmesi, c) polimerizasyon prosesi için miniemülsiyon ortamının oluşturulması ve kontollü/yaşayan polimerizasyonun miniemülsiyon ortamında gerçekleştirilmesi aşamalarından oluşmaktadır. İlk olarak azo grubu içeren ACPA'dan ACPC sentezi gerçekleştirilerek keten yağından gliseroliz reaksiyonu ile elde edilen kısmi gliseridlerin ACPC ile esterifikasyonu sonucu yağ temelli makrobaşlatıcı sentezlenmiştir. Yağ temelli makrobaşlatıcının stirenlenmesi prosesinde, ultrasonikasyon işleminin ardından, belirli makrobaşlatıcı:nitroksit ajan oranında (1:1), ideal miniemülsiyon koşullarını belirlenmek üzere miniemülsiyon polimerizasyonu farklı surfaktan (DOWFAX 8390) miktarlarıyla gerçekleştirilmiştir. Ürün dönüşümleri gravimetrik olarak hesaplanarak molekül ağırlıkları GPC analiziyle belirlenmiş, ürün ve ara ürünlere ait yapısal karakterizasyonlar FT-IR ve ^{1}H-NMR spektroskopileri ile belirlenmiştir. Çözücü ortamında da nitroksit ajan varlığında makrobaşlatıcının stirenlenmesi prosesi gerçekleştirilerek, miniemülsiyon polimerizasyon ortamının etkisi irdelenmiştir. Elde edilen yağ ürünlerinin film özellikleri ilgili standartlara göre test edilmiştir. Sonuç olarak, NMRP yöntemi ile kolloidal kararlılığı sağlayarak miniemülsiyon koşullarında stirenleme işlemi başarılı bir şekilde gerçekleştirilebilmiş ve bu yöntemle elde edilen numuneler düşük PDI değerleri ve iyi film özellikleri sergilemiştir.

Tez kapsamında stirenleme prosesi, hava üflenmiş keten yağının RAFT tekniği ile, kısmi gliseridlerden elde edilen makroazobaşlatıcının da NMRP tekniği ile miniemülsiyon koşullarında stirenlenmesi ile gerçekleştirilmiştir. Böylece, prosesin organik çözücü kullanımından kaynaklanacak maliyet ve çevresel etkileri gideren su ortamında gerçekleştirilmesi, kontrollü/yaşayan polimerizasyon teknikleri kullanılarak hem stirenin homopolimerizasyonunun önlenmesi hem de kontrol edilebilen molekül ağırlığına sahip, düşük polidispersitede, klasik yöntemlerle gerçekleştirilen ürünlere göre daha iyi film özelliklerine sahip stirenlenmiş yağ örneklerinin hazırlanması başarılmıştır. Stirenleme işleminin su ortamında gerçekleştirilerek iyi film özelliklerine sahip kopolimerlerin elde edilmesi, su ortamında düşük molekül ağırlığı dağılımı sağlanması ve aynı zamanda kontrollü radikal polimerizasyonunun miniemülsiyon şartlarında gerçekleştirilmesi yaklaşımı çalışmanın özgün değerlerini ortaya koymaktadır.

Tez çalışması, doğal ve sentetik kaynakların birleştirilerek iyi özellikte yüzey koruyucu malzeme üretimi ile, endüstriyel/geleneksel proses koşulları ve korozyon yoluyla oluşacak maddi kayıpların önüne geçildiğinden hem çevre hem de kaynakların kullanımı açısından önem arzetmektedir. Son yıllarda istenen molekül ağırlığı ve moleküler geometride polimerizasyon işlemlerini mümkün kılan kontrollü/yaşayan radikal polimerizasyon yöntemlerinin su ortamında gerçekleştirildiği çalışmalarda emülsiyon-miniemülsiyon şartlarının ve kontrollü radikal polimerizasyonu ajanlarının davranışı ve su ortamında polimerizasyon kinetiği ilgi çeken, yoğunlaşılan noktalar olmakla beraber, elde edilen ürünlerin endüstriyel uygulama hedefi olmaması bu çalışmanın literatürde de orijinalliğini öne çıkarmaktadır. Hem söz konusu bu çalışmalarda konu edilen kontrollü radikal polimerizasyonu yöntemlerinin adapte edildiği basit polimerizasyon proseslerinin

(polistiren, PMMA gibi) ötesinde su ortamında yağ/stiren kopolimerizasyonunun gerçekleştirilmesi, hem de elde edilen nihai ürünlerin uygulama alanı bulması çalışmanın ulusal/uluslararası akademik/endüstriyel katkısını açıkça ortaya koymaktadır.

1. INTRODUCTION

Triglyceride oils have been used as an ingredient for organic coating formulations for years and they are usually modified by various methods for better film performances. For the modification purpose, physical and chemical strategies were applied, the latter being widely applied by using vinyl and non-vinyl monomers [1-5]. Among the vinyl monomers, styrene was extensively used to produce styrenated oil [1-5]. For the preparation of the styrenated oil, actually known for years [1, 2, 5], the mixture of styrene and oil is heated at a high temperature and styrene attaches to the oil molecule through the radicals formed on the fatty acid chain. This polymerization was also carried out in a solvent medium in order to increase the copolymerization yields. In this classical styrenation process, homopolymerization of styrene is more likely to occur, consequently much amount of oil moeity uncombined to the styrene chain remains in the product. Due to this fact, the resulting styrenated oil gives an undesired opaque film. In order to increase the amount of oil moiety in the copolymer structure, mainly two strategies were applied. For this purpose, macroinitiator and macromer methods were developed [5-16]. In the macroinitiator method, the thermoliable azo groups were inserted into the oil molecule, and styrene was combined through radicals formed by thermal decomposition of the azo groups. The styrenated oil obtained by this strategy gave a clear film indicating that homopolymerization was appreciably prevented [5-9]. Another strategy developed was to insert vinyl groups to the oil structure in order to obtain a macromer. In this way, the macromer was copolymerized with styrene under the conditions of free radical polymerization. This route was also result in a clear film of the styrenated oil samples [9-12]. In order to control the molecular weight distribution, a regenerative chain transfer agent was also used [5]. Macromer and macroinitiator methods were carried out under the conditions of controlled living radical polymerization such as nitroxide mediated radical polymerization (NMRP) [13, 14] and reversible addition-fragmentation chain transfer (RAFT) polymerization techniques [15, 16]. In these

ways the copolymer products with low molecular weight distribution and with good film properties could be obtained.

RAFT polymerization is one of the most versatile methods of controlled/living free radical polymerization and has been well established in homogeneous polymerization systems, such as bulk or solution polymerization [17-20]. Although RAFT polymerization in emulsion has been of particular interest, a few problems such as high levels of coagulum, very slow polymerization rates, thick red layers depends on phase separation and loss of molecular weight control have been reported in RAFT emulsion systems [21-25]. In order to eliminate these problems, researchers focused on the applications of RAFT polymerization miniemulsion and microemulsion systems [26-29]. Liu and co-workers studied RAFT polymerization of n-hexyl methacrylate for the first time in microemulsion and compared the results with those of conventional microemulsion polymerization. They reported that the RAFT technique could be successfully used in microemulsion system and more stable latex particles even in the range of 18-30 nm size could be obtained [28]. From the literature survey, it was understood that there are a number of successfully completed studies on the RAFT mediated aqueous media polymerization of styrene [26, 30, 31], methyl metacrylate [27, 32], vinyl acetate [33] and fluoroacrylates [29].

Although the research studies on CLRP techniques are focused on homogeneous systems such as solution and bulk polymerization [34-42], the CLRP adapted emulsion and mini/micro emulsion systems also have been attracting attention in recent years [21-30, 43-49]. In early applications of NMRP in macroemulsion system were not so successfull because the preservation of the living characteristics of the polymerization and the elimination of the over sized particles could not be achieved [45]. These unsuccessfulness arised from using unsuitable surfactants and nitroxide components in the macroemulsion polymerization. Since NMRP systems are realized relatively at a high temperature (120-135 ^{o}C), the traditional surfactants such CTAB, SDS, *etc*. decomposed and caused colloidal instability [45, 47]. Since the surfactants such as DOWFAX 8390 and SDBS are more stable at temperature about 135 ^{o}C, they were used in the later studies on NMRP macroemulsion polymerization [45-48]. In order to have a good colloidal stability, apart from surfactant, unimer initiating systems were also investigated instead of bicomponent initiating system. In the case of unimer, since initiator is in the oil droplet, even at the beginning, the

polymerization occurs to a great extent in the droplets [45]. Additionally, the solubility of the nitroxide component in water and oil phases should be suitable for the applied polymerization. Otherwise the polymerization can not be controlled [45, 47]. The NMRP adapted miniemulsion polymerization includes different types of initiating systems such as bicomponent and alkoxyamine systems with oil/water soluble initiators [50]. As it is known, in the miniemulsion polymerization, the monomer droplets act as a nanoreactor. In this way, a bicomponent system with an oil soluble initiator is quitely effective for a miniemulsion process. Prodpran et al. reported a succesful NMRP adapted miniemulsion polymerization of styrene by using TEMPO radical, benzoil peroxide (BPO), as an oil soluble initiator, and Doxfax 9380 as surfactant with bicomponent initiating system [51]. Furthermore, when a water soluble initiator was used in the same system, TEMPO/KPS ratio was reported to be important and high monomer conversion and low PDI values were obtained with an optimized TEMPO/KPS initial ratio [52].

Actually, in the past for the purpose of waterborne binder preparation oil, alkyd and acrylic contents were used. Van Es et al. utilized hydroperoxides of triglycerides as initiator for miniemulsion polymerization of acrylates in a Fe(II)/EDTA/SFS redox system. They explained that t-butyl hydroperoxide with the same redox system, cause to phase separation while sunflower hydroperoxide resulted in homogeneous particle [53]. Schork and co-workers studied limited monomer conversion encountered in the miniemulsion polymerization of unsaturated alkyd resin and acrylic monomer system [54]. Schork et al. studied the polymerization of acrylate-alkyd hybrid latex system under miniemulsion conditions in order to solve the poor homogeneity of the particles due to the immiscibility of the components. They carried out the polymerization in the presence of linoleic acid and sunflower seed oil. It was understood that this application enhanced the homogeneity of the hybrid polymer particles in waterborne latex system [55]. Heiskanen et al. prepared hybrids of alkyd resin and acrylics with different alkyd/acrylic ratios by classical emulsion polymerization. Their results showed that the alkyd/acrylic hybrids with synergistic and improved film properties could be prepared [56].

In the first part of the thesis, controlled/living radical polymerization was further carried out under the miniemulsion conditions. For this purpose air-blown linseed oil-styrene system having large amount of hydrophobic oil moeity was subjected to

RAFT polymerization in the miniemulsion medium in the presence of phenacyl morpholine dithiocarbamate (PMDC) as a RAFT agent. The resulting styrenated oil sample was investigated in view of molecular weight, polydispersity index and film properties. The styrenated oil obtained in this way has a molecular weight distribution lower than that of the sample of classical RAFT polymerization carried out in dioxane. In the end, the film properties of the obtained styrenated oil samples were determined. In the second part of the thesis, styrenated oil preparation was performed by NMRP adapted miniemulsion polymerization because of its benefits over classical emulsion polymerization. The ingredients of the polymerization carried out in this study were water insoluble and their incorporation into the polymer backbone was favored under miniemulsion condition. In this way, it was aimed to eliminate the problems of colloidal instability to a great extent encountered in macroemulsion polymerization. It is well known that, in the miniemulsion polymerization, the droplets are so small that they compete for the radical entry and, consequently, they become a 'nanoreactor' where the polymerization takes place [50].

In this study, a new strategy was applied for determining the best conditions for miniemulsion polymerization. In order to understand whether the polymerization was miniemulsion or not, in literature, the widespread way was to measure the droplet/particle size at the beginning and/or at the end of the polymerization. If the droplet/particle size was within the size of miniemulsion, the polymerization was accepted as a miniemulsion polymerization. However, this procedure could not guarantee that the polymerization was carried out under the best conditions for miniemulsion polymerization. By taking this fact into account, a new strategy was applied for determining the optimum conditions of miniemulsion polymerization. Thus, by applying this strategy, the conditions of being 1:1 copy for the droplets [45, 50] throughout the polymerization were determined. Finally, the styrenated oil sample prepared under the determined best miniemulsion conditions was investigated in view of molecular weight, PDI and film properties. The styrenated oil thus obtained had a molecular weight distribution lower than that of classical CLRP polymerization in solvent. In the end, the film properties of the styrenated oil samples were determined. The results showed that the prepared styrenated oil products could be used successfully as an oil based binder.

critical micelle concentration (CMC) is defined. In emulsion polymerization systems, concentration of surfactant should be above the CMC. Surfactant forms micelles at this concentration level [50, 57].

Classical emulsion polymerization has mainly three nucleation mechanisms such as homogenous nucleation, droplet nucleation and micellar nucleation. These nucleation mechanisms define the loci of polymerization. Polymerization can be take place in monomer droplets (droplet nucleation), in water phase within the micelles (micellar nucleation) which form above the CMC of system and directly in water (homogenous nucleation). Nevertheless, droplet nucleation and homogenous nucleation are quitely limited compared to the micellar nucleation. Monomers are low water soluble so homogenous nucleation is greatly inhibited. Additionally, monomer droplets, which have smaller total surface area compared to the micelles, also do not provide polymerization medium because the negatively charged initiator anions find these monomer droplets actually impossible to diffuse [47-49].

Classical emulsion polymerization kinetics can be examined in three stages. In the first stage particle formation occurs due to the increase of the polymerization rate and the amount of particle. At this stage, approximately 10-20 % conversion is observed and micelles are converted to the monomer-swollen particle. The monomer conversion is due to the surfactant type, surfactant concentration, monomer solubility (in water) and the initiation rate. At the end of the first stage, inactive micelles which are without the particles dissappear and become unstable. After the disappearence of inactive micelles at stage 1, polymerization takes place in monomer-swollen particles. At the second stage, diffusion of monomers from monomer droplets occurs and monomer droplets act as monomer reservoirs. Monomer droplets becomes smaller and the size of polymer particles grows due to the diffusion of monomers from droplets. When particle nucleation is completed, polymer particles and the rate of the polymerization become constant. This stage ends when all monomer droplets are exhausted. The conversion reaches nearly 20-50 % at the end of this stage. At the last stage, there is no dissolved monomer, monomer droplets, micelles and dissolved surfactant in the reaction medium. Monomers are fully associated with polymer particles. Due to the disappearence of all monomer droplets, polymerization takes place only with the monomer exhaustion of particles. At the end of the stage 3, about 50-80 % conversion was reached [57, 58].

The schematic representation of the stages, which defines the kinetics of emulsion polymerization, is given in Figure 2.2.

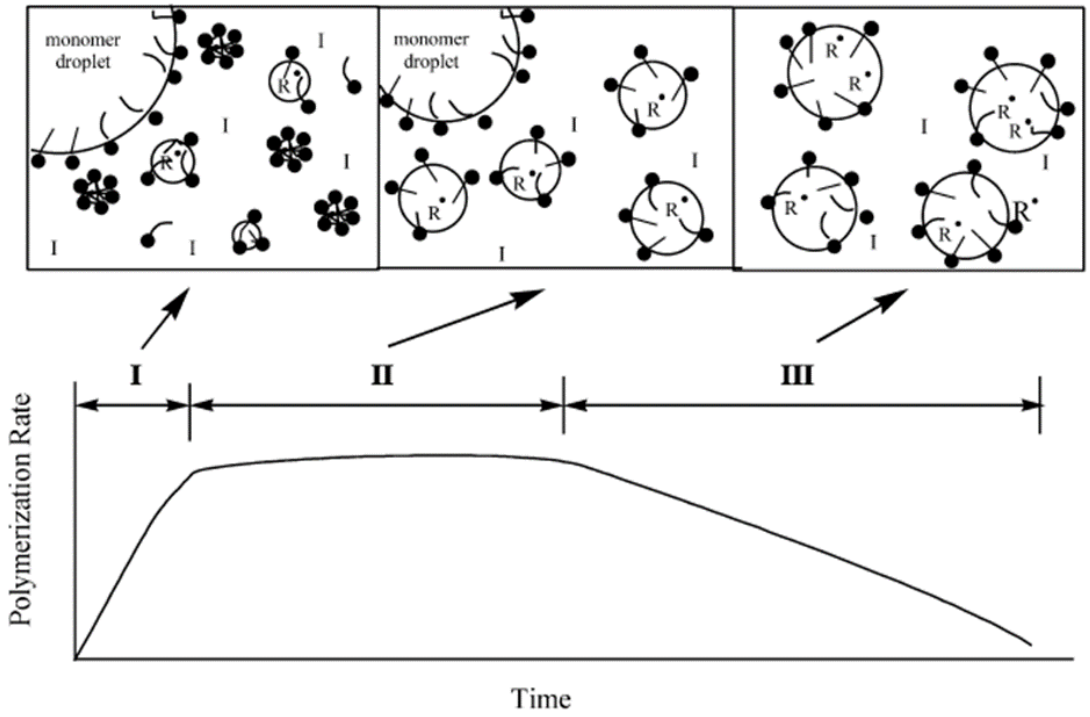


Figure 2.2 : The stages of the emulsion polymerization kinetics [59].

Advantages:

- High heat capacity and the ease of stirring of the water (continuous phase) minimize the thermal and viscosity problems.
- High molecular weight polymer products can be produced.
- Viscosity of polymer is independent of the molecular weight.
- Heat exchange medium (water) is economic, nonflammable, nontoxic compared to solution polymerization (organic solvents).

Disadvantages:

- The ingredients (emulsifiers and others) in the system compose undesirable contamination to the polymer products.
- Additional operations (the separation of the polymer from dispersing media and purification) are required for good quality polymer products [50, 57-59].

2.1.4 Suspension polymerization

The suspension polymerization technique is commercially used for production of many polymers such as poly(methyl methacrylate), poly(vinyl chloride), poly(vinyl acetate), poly(vinylidene chloride), polystyrene, many types of resin including

polystyrene and poly(styrene-acrylonitrile) copolymer. The porous and non-porous polymer particles, which are 50-1000 micrometers in diameter, can be obtained depending on the reaction conditions. A typical suspension polymerization system contains two phase: monomer phase and dispersing phase. Oil-soluble monomers are diffused in dispersing phase as liquid droplets by stirring and surface-active agents (surfactant) are not used in suspension polymerization unlike an emulsion system. Suspension polymerization has a basic nucleation mechanism compared to emulsion polymerization. The monomer droplets containing dissolved initiator are dispersed in water phase and polymerization occurs inside these droplets. The diameter of the polymer particles in the suspension depends on the viscosity of phases, stirring speed, monomer: water ratio and the type and concentration of the stabilizer [57, 59].

In an effective suspension polymerization system, the solubility of monomer in dispersing phase should be very low. For this purpose, the hydrophobic liquid phases such as oil and petroleum ether are used for the polymerization of hydrophilic monomers and water is also the dispersing media for the polymerization of hydrophobic monomers.

Advantages:

- Heat exchange medium (water) is more economic, nonflammable and nontoxic compared to solution polymerization (organic solvents).
- Viscosity is low due to the suspension.
- Excessive heat removal is easy due to the high heat capacity of water.
- Control of temperature is relatively simple.
- Separation and purification of polymer product is relatively easier than in emulsion polymerization.

Disadvantages:

- Polymers have glass transition temperature which is less than the polymerization temperature can not be polymerized.
- Separation and purification are needed for good-quality polymer products [57, 59].

2.1.5 Miniemulsion polymerization

Miniemulsion polymerization method has several advantages compared to conventional emulsion polymerization. In this polymerization technique, monomer diffusion from droplets to aqueous phase is prevented and droplet nucleation allows polymerizing water insoluble monomers. Due to this fact, in a miniemulsion process, polymerization directly occurs in monomer droplets. Shearing forces initially create monomer droplets and a mechanical energy process such as ultrasonication is necessary for initial miniemulsion generation. Miniemulsion process need a lower surfactant content while in conventional emulsion polymerization surfactant concentration should be above CMC. Cosurfactant (or costabilizer) is used to prevent Ostwalt ripening effect to achieve the droplet stability. [50, 59].

In contrast to complex nucleation mechanism in emulsion polymerization, in ideal miniemulsion process, polymerization occurs directly in the monomer droplets initially formed by shearing forces. Unlike conventional emulsion polymerization, the need of surfactant in the miniemulsion process is less. The micelle formation and micellar nucleation, which are predominant in the emulsion polymerization, are inhibited. The inhibition of micellar nucleation also makes the mechanism of particle formation in the miniemulsion polymerization different. In this way, the disadvantages of emulsion polymerization such as the need of high levels of surfactant and initiator, high polymerization temperature, and limited type of monomer to be used are also eliminated [59].

The adaptation of the miniemulsion polymerization to the controlled/living radical polymerization techniques is very convenient. Unlike emulsion polymerization, colloidal stability is better in the miniemulsion polymerization. For this reason, miniemulsion polymerization may be preferred in the synthesis of polymers with the desired molecular weight and low polydispersity.

Representative stages of a miniemulsion polymerization process and the miniemulsion polymerization mechanism are seen in Figure 2.3. The surfactant and cosurfactant are added to the water phase together with the monomer to form the minemulsion before the polymerization reaction. This miniemulsion mixture, which consists of organic and inorganic phases, is subjected to a shear force.

Ostwald ripening effect observed in the miniemulsion polymerization indicates that the transfer of monomers from small droplets to large droplets is achieved. When Ostwald ripening effect occurs predominantly, creaming occurs in the polymerization medium. The addition of cosurfactants such as hexadecane to the reaction medium prevents this effect and transfer between the droplets. When this property is taken into consideration, the addition of the cosurfactant to the reaction medium prevents the conversion of the miniemulsion into emulsion, but the addition of cosurfactant to the emulsion does not convert the emulsion into a miniemulsion. This effect is achieved only by the addition of the costabilizer to emulsion mixture, followed by the formation of a miniemulsion with high energy by ultrasonication process [50, 59].

Anionic surfactants such as sodium dodecyl sulphate (SDS) are generally used in the miniemulsion polymerization because they are compatible with many types of initiators and monomers. Nonionic surfactants are preferred in some controlled radical polymerization applications since anionic surfactants are not suitable. It has also been observed that the cationic surfactants such as cetyltrimethylammonium bromide (CTAB) are used under the polymerization conditions and the products obtained in this way had similar characteristics compared to the products obtained by polymerization carried out with anionic surfactants. An important parameter in choosing cosurfactant is that it should be water-insoluble and monomer-soluble. It is also expected to use cosurfactant has low molecular weight at the same time. Water-insoluble properties also prevent transfer of monomer to the water phase from monomer droplets. The use of cosurfactant with low molecular weight makes it possible to increase the weight ratio of cosurfactants to monomers in monomer droplets and thus to achieve a more efficient process condition. However, these cosurfactants may be volatile under natural conditions and their presence in the products obtained may not be desirable. In such cases, non-volatile cosurfactants are used. On the other hand, it is known that polymers that are soluble in their own monomer are used as a cosurfactant when the presence of cosurfactant is not desirable in polymer product. Chain transfer agents can also be used as a costabilizer. Generally, in conventional emulsion polymerization, it is difficult to transfer chain transfer agents to water-borne particles from monomer droplets. However, the chain transfer agent may be preferred as the cosurfactant only in the case of the

miniemulsion conditions in which polymerization takes place in monomer droplets [50].

It is known that both oil and water-soluble initiators are used in the miniemulsion polymerization. The most widely used water-soluble initiator is KPS. The oil-soluble initiators are listed as AIBN, BPO and LPO. Very small changes in the average droplet size after sonication have been observed in the case of oil-soluble initiators in the miniemulsion polymerization. When a costabilizer such as hexadecane is added to the reaction medium, the size distribution is almost constant and it is not depend on which initiator is used [50, 59].

2.2 Oil and Oil Derivatives

Polymers are material groups obtained from natural and synthetic sources. Because the synthetic polymers are not environmentally friendly as they are being exposed to the biodegradation process, the development of biodegradable and environmentally friendly polymers is an urgent requirement. Moreover, the rapid consumption of natural petroleum sources also verifies this requirement. These problems and limitations have directed the scientists to investigate the new alternative sources having significant features such as environmental sustainability and biodegradability for the plastic materials. The vegetable oils and other lipids are also seen as sources of these alternative materials. Natural and modified oils are useful for the production of polymers with significant functional properties [60].

Triglycerides are defined as renewable natural sources, and they are significant starting substance for the production of biodegradable polymers. For example, triglyceride oils such as flax oil and tung oil are used as polymer source due to the double bonds in their structures and their functional groups causing polymerization. The double bonds of triglyceride oils are able to give epoxide structures in order to increase their reactivity, or they are being transformed to hydroxyl groups. Only a few oils naturally include special functional groups such as hydroxy or epoxy. The C=C double bonds in the structure of oils are being used through chain growth mechanism in order to form the polymerized plastics. Moreover, the hydroxyl or epoxide functional groups are making the oils important as they can be polymerized with suitable bifunctional reactants as to form polymer. By these properties, the oils

grams) that reacts with 100 grams of oil. By the determination of the iodine number, it is possible to estimate the oxidative drying capacity of an oil. High iodine number values indicate excessive unsaturated bond, and low iodine numbers indicate less unsaturated bond. They are divided to three levels as being drying oils (with an iodine index over 130), semi drying oils (with an iodine index in between 90-130) and non-drying oils (with an iodine index under 90) as per their technical properties. [70, 71].

Drying is the oxygen holding ability of the oil. The type of unsaturation also affects the drying time of oils. The drying properties and reactivity of glycerides consisting of conjugated unsaturated fatty acids are better compared to drying properties and reactivity of fatty acids including isolated double bond. Conjugated double bond is accelerating the oxidative drying process [70, 71]. The best-known types of oils can be defined as follows in the context of drying properties.

Sunflower oil: It includes low proportion of linolenic acid, and high level of linoleic acid.

Linseed oil: The unsaturated linoleic and linolenic acid contents are high in linseed oil. Linseed oil has a very good drying property, and the films it forms have perfect resistance against exterior atmospheric conditions. Its resistance to weak acids and bases is good, and its water permeability is very high. Linseed oil has very good pigment wetting property. Its films turn yellow due to its linolenic acid ratio of about 50%.

Castor oil: Castor oil shows non-drying oil property before removing water. Thus, it is used as plasticizer in alkid resins and ink formulations. The castor oil includes 87% ricinoleic acid and 12% oleic acid. The castor oil is heated up to 270^{o}C by using inert gas with the catalyst, and conjugated double bonds arise by the removal of one mol water.

China wood oil: 80% of the fatty acids in china wood oil are eleostearic acid including conjugated double bonds. For this reason, it exhibits quick drying properties. As it dries very fast, the arising film is not smooth but creased. The process is carried out in the alkid resin manufacture along with inert gas. Otherwise, it faces rapid polymerization with heat and oxygen.

2.2.2.1 Drying oils

Numerous double bonds exist in drying oils. They solidify in air. These double bonds react with the oxygen, and it enables it to solidify by ruining the structure of the compound. In isolated double bond position, there are one or more methyl groups among the unsaturated groups (double bonds) within the carbon chain of the fatty acid. In conjugated double bond position, there is no methyl group among the unsaturated groups (double bonds) in fatty acid and in cumulative double bond position, there are two carbon atoms including three double bonds within the carbon chain of fatty acid [67-71].

2.2.2.2 Semi drying oils

When they are applied on a surface not having absorption property, they form a film in a much longer period. However, this film does not provide the sufficient film hardness for the dye, and it shows softness and elasticity (sunflower oil, soybean oil, opium oil, corn oil). The semi drying oils such as soybean oil consist of acids including only one or two double bonds [70, 71].

2.2.2.3 Non drying oils

These type of oils such as olive oil, palm oil, castor oil do not form any film even after a long period when they are applied on a surface not having absorption property. The non-drying oils such as castor oil consist of glycerides of saturated fatty acids not having drying property, or they include a very small amount of a single double bond acid [71].

2.2.3 Drying process

“Linoleic acid” within the oils includes isolated double bond, and “eleostearic acid” within the oils includes conjugated double bond. The oils including these two fatty acids play a significant role in the manufacture of coating materials. The flexibility, durability, resistance against external factors, color and brightness of oils and fatty acids including conjugated double bond may be improved as subjecting them to various modifications. The number of cross-links formed increase as much as the number of double bonds and the properties of the film change. If most of double bonds have conjugated structure, their drying time decrease. The drying time increases if the ratio of isolated double bonds is high. When there are fatty acids that

include at least two double bonds, the oil will give reaction by taking oxygen from the air in order to form the cross-link nets. The drying oils form films providing touch drying. In addition, the semi drying oils do not provide touch drying. The ability of an oil to react with oxygen by itself without any addition is called as 'autooxidation'. The semi drying and drying oils are very sensitive against oxygen, and they are forming film as solidifying in time through autooxidation. This film formation is an irreversible process. This process is called as drying process [70, 71]. The chemical reactions in the drying process are very complex, but a significant part of them is reactions in the double bonds of unsaturated glycerides and reaction with the atmospheric oxygen. The processes in the drying are highly being affected from temperature. Polymerization is more effective at high temperatures compared to low temperatures. The main process at low temperatures is oxidation. The rate of reaction depends on reaction conditions such as temperature, light, heavy metals and inhibitors in the oil or coating [70].

The linseed oil includes linolenic acid is an example of non-conjugated oil. In non-conjugated oils, the linolenic acid content plays a significant role in the drying process, because in these systems the autooxidation process is starting with the dehydrogenation of the unsaturated fatty acids –such as linolenic acid- with the atmospheric oxygen. Consequently, dehydrogenated radicals are forming. The chain polymerization is stating with the formation of hydroperoxides. Moreover, crosslinking is arising in order to form large molecules. Drying, crosslinking and polymerization are realizing in drying oils due to the double bonds and unsaturated centers within the structure of fatty acids [70, 71].

The chemical mechanism of drying can be classified in four steps as induction period, formation of peroxide, decomposition of peroxide and polymerization. Induction period is the period by the beginning of the reaction where no physical and chemical change is observed in oil. The induction period is slow at the beginning, but it is an autocatalytic reaction, and reaction rate gradually increases. After the induction period, formation of peroxide is the second stage that the oxygen is absorbed on the carbon atoms near its ethylenic groups in order to form the hydroperoxide and holding of oxygen arises at a high degree. In the third stage, decomposition of hydroperoxide, these hydroperoxides are then exposed to a serial reaction in order to provide compounds including short chain carboxylic acids. In

order to form high free radical concentration, the hydroperoxides start to decompose, and the reaction realizes as autocatalytic. The last stage is polymerization. The free radicals cause polymerization through crosslinking among double bonds. Polymerization starts and crosslinked products with high molecular weight, carbonyl/hydroxyl compounds, carbon dioxide and water are formed [70, 71].

Tung oil is an example of conjugated oils and it substantially includes eleostearic acid. Conjugated oils are more inclined to polymerization and oxidation compared to non-conjugated oils. The drying of conjugated systems includes the following steps;

Induction: This process starts with the autocatalysis of eleostearic acid. Oxygen intake starts to gradually increase.

Initiation: The film continues to absorb oxygen from the atmosphere and as the result of absorption the mass of the film increases and the double bonds of eleostearic acid are exposed re-arrangement process. By this arrangement, hydroxyl and hydroperoxide groups are formed on the film structure.

Crosslinking: Following the above two steps, the number of double bonds decreases due to crosslinking, and thus larger molecule forms.

In order to accelerate the oxidative drying period, and especially the oxygen absorption and polymerization step, drying agent is able to be added in the dye. These agents are called as dryers, and they are used in dyes at room temperature or at high temperatures in order to optimize the drying of resins. The dryers are carboxylate derivatives of different metals. The effect of drying metals does not stop even when the film dries, it continues along the lifetime of the film, and thus it contributes to the final brittleness. The drying effect of the metal does not depend on the form of the acid radical when complete dissolution of metal is ensured in dye [70].

2.2.3.1 Dryers

Dryers decrease the induction period, increase the oxygen absorption rate, assist the formation and decomposition of peroxides and decrease the required oxygen amount. Dryers are classified as oxidation catalysts, polymerization catalysts and auxilary catalyst.

Oxidation catalysts: These dryers are called as primer dryers, and they assist the oxygen absorption of dye film and the formation and decomposition of peroxides. The best oxidation catalyst is cobalt based dryer.

Polymerization catalysts: They are the secondary dryers. They assist the drying of dye film. They include lead and zirconium.

Auxiliary catalysts: They are calcium, lithium, potassium and zinc based catalysts [70].

2.2.3.2 Modification of drying oils

Various methods are applied to improve the drying properties of oils.

Decomposition: The oil is treated with a solvent that do not completely mix with it. Two different layers are being formed due to the differences in the ratio of oil and solvent. It is ensured to partially decompose the unsaturated glycerides from the saturated ones. This decomposition reflects the drying periods. While a fraction dries more rapidly, the other one dries more slowly. By the repetition of the process on the fractions, higher decomposition of glycerides is able to be ensured.

Reaction with unsaturated compounds: The most widespread unsaturated compounds being used are maleic anhydride and styrene. Styrene is able to be heated up in order to provide the required products with the unsaturated oils. The oils subjected to styrene dry fast in order to provide a hard film.

Mono and diglycerides of oil acids: Mono and diglycerides are normally available in naturally drying oils. However, they can be prepared by various operations. For example, the oil is being heated up with glycerol in the presence of catalyst under inert atmosphere. The product obtained as the result of this operation is the mixture of mono-, di- and unchanging triglyceride. Monoglycerides are more important. These glycerides are used as plasticizers. The main usage of monoglycerides is in the production of alkids. The two free hydroxyl radical in their structure is easily esterified [70, 71].

2.3 Controlled/Living Radical Polymerization (CLRP)

Classic radical polymerization has been considered as one of the broadest and most widespread methods used for polymer synthesis. Many commercial polymers are

generated by conventional radical polymerization. Low-density polyethylene, PVC, polystyrene and its copolymers, polyacrylates, polyacrylamides, polyvinyl acetate, polyvinyl alcohol and fluoropolymers are the most significant ones among these products. These commercial polymers and copolymers are prepared with radical polymerization due to simple reaction conditions, wider temperature range and ease of polymerization [72]. There are many important differences between classical radical polymerization and CLRP even though they progress through the same radical mechanism. In classical radical polymerization initiaton step is very slow and initiator is generally not completely exhausted. However, in most CLRP systems initiation is very fast. So, the most important requirements in order to reach the properties of living polymerization are the high rate of initiation reaction compared to rate of growth reaction, lack of termination and transfer reactions. Nevertheless, in classic free radical polymerization, initiation is slow compared to growth velocity, and it is hard to abstain from bimolecular termination reactions among the radicals. Thus, while new radicals are forming along the whole polymerization process, non-living polymers with high molecular weight are forming in the initial phases of the polymerization, and consequently the molecular weight distribution is being wide. While in the radical polymerization all chains are almost dead, the dead chain ratio in CLRP is quite low (> %10). In radical polymerization, the termination step usually proceeds between long chains and new chains obtained. In CLRP systems, all chains are short at the beginning of the reaction and extend over time. Termination spontaneously occurs by the consumption of monomers [72, 73]. Compared to conventional free radical polymerization, CLRP techniques provide reversible activation and deactivation balance between inactive and active chains. With this balance, all polymer chains grow simultaneously at the same rate. Molecular weight and molecular weight distribution control is provided by reducing irreversible termination in CLRP techniques operate based on the principle of dynamic balance established in between inactive and active types (growing free radicals) [74, 75].

Several important parameters should be observed in a successful controlled/living polymerization system. These can be listed as follows: 1) logarithmic conversion should be linear correction to the time, 2) the molecular weight (Mn) should show a linear relationship with the increased monomer conversion, 3) low molecular weight distributions (PDI) should be observed.

Therefore, only a small amount of continuously occurring chains does not contribute to the total chain number so that a good control can be obtained over molecular weight. RAFT mechanism generally consists of five steps. General RAFT mechanism is given in Figure 2.8.

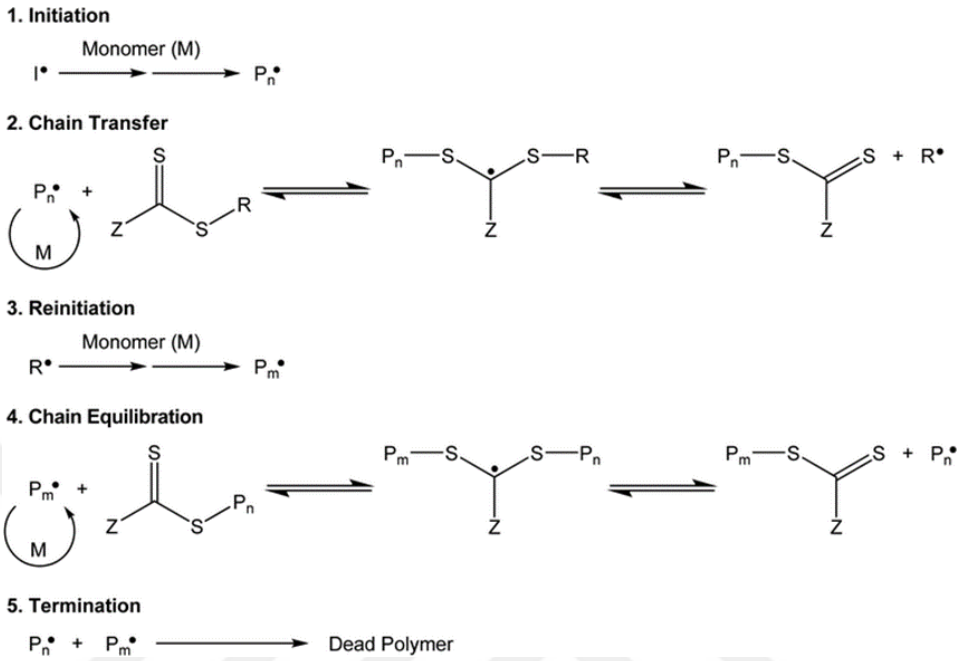


Figure 2.8 : General mechanism of RAFT polymerization.

Initiation: This step starts by using initiators similar to other radical polymerization reactions. AIBN and peroxide initiators are used. The most commonly used ones are azo initiators. At the beginning step, initiator forms a radical group by reacting with monomer and ensures the starting of the active polymer chain [17, 18, 84].

Propagation: RAFT agents, also known as transfer agents are used in this step. These substances are thio carbonylthio compounds and they contain two different functional groups in their structures. The polymer chains begin to form on Z and R groups which are on RAFT agent. These two functional groups have different functions. The function of –Z group is to provide the easy connection of the radical groups with the thiocarbonyl C=S bond. On the other hand, -R group has a very important function. New monomers can be added to between S-R bond and initiating a new polymer chain is made possible. Reversible chain transfer mechanism can only proceed with optimal activity of these two groups [17, 18, 84].

Re-initiation: The leaving group (-R•) released after the reaction ensures another active polymer chain by reacting with one of the monomers in the reaction medium. This active chain obtained in this step will be exposed on its own to growth-

fragmentation and balancing steps. This happens with the adding of the new radical (R·) to monomer reaction (Pm·) [17, 18].

RAFT equilibrium: The catching of the growing active radical groups by Pm· and Pn· inactive or stable thiocarbonyl compounds forms the most basic step of RAFT polymerization, balancing. Thus, chain termination step seen in conventional radical polymerization is not seen in this system. Actively growing radicals (Pn· and Pm·) and dominant polymeric thio carbonyl thio compounds provide equal opportunities for the growth of all the chains and makes the production of polymers with narrow molecular weight distribution possible [18, 85].

Termination: There is no termination in RAFT but there can only be with an exterior impact. The termination step of the RAFT polymerization is suppressed by reducing the radical concentration. Therefore, in order to obtain inactive chains after the reaction, to terminate the reaction, outside control is always necessary [18, 85, 86].

2.3.3 Nitroxide mediated radical polymerization (NMRP)

The polymerization is carried out by the addition of a stable free nitroxide radical to the reaction medium. In addition, the stability of the stable free nitroxide radical depends on the electronic structure of the radical. Delocalization of electron, which is not paired on the N-O bond, provides thermodynamic stability to the radical. In the polymerization system, the nitroxide radical acts as the trapping substance and it forms a loose bond by combining with the other growing radicals. This bond is being exposed to homolytic disintegration as reversible at higher temperatures. Moreover, as these stable radicals prefer to react with growing carbon centered radicals rather than monomers; the reversible closer reaction severely decreases the radical concentration by the end of the chain. As the termination reaction is minimized due to this decreasing radical concentration, the character of living polymerization gains importance [87].

The basis of the NMRP mechanism is the reversible deactivation of the active polymer radicals with a stable nitroxide radical such as TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) in order to form an alcoxyamin. In this system, the growth of polymers is realized in a controlled manner. The monomer is added to the polymer radicals among the successively arising activation and deactivation reactions. The balance reaction is enabling the formation of substantially ineffective

alcoxyamins. In this case, the concentration of active radicals is lower than the classic free radical polymerization. Consequently, as termination is of second degree compared to the concentration of active radicals, the velocity of bimolecular radical termination is minimized more than the velocity of growth. Under these conditions, the polymer radicals grow in living style, and the generation of polymers with polydispersity and with molecular weights that can be estimated in advance is being possible [88, 89].

Typical NMRP polymerization can be carried out by different methods varying according to the initiating systems. These methods are known as bicomponent initiating system and monocomponent initiating systems. In bicomponent initiating systems, free nitroxide radicals and classical initiators are used. Monocomponent systems are carried out with alkoxyamine structures and radical-terminated polymers. The first studies carried out by NMRP are about the polymerization of styrene in the presence of TEMPO nitroxide radical [90, 91, 92]. In subsequent studies, different nitroxide radicals have been used in the polymerization of monomers such as styrene, methacrylate, n-butyl methacrylate for more controlled reactions [93, 94, 95].

2.4 CLRP in Heterogeneous Systems

2.4.1 ATRP in emulsion polymerization

Atom transfer radical emulsion polymerization, which is one of the living free radical polymerization techniques, can be successfully be applied into suspension, emulsion and miniemulsion [96-99]. A typically ATRP can be determined with the study of Gaynor et al. that they investigated the ATRP of n-butyl methacrylate (n-BmA) initiated with ethyl 2-bromoisobutyrate (EBiB) in the presence of CuBr as a catalyst and dNbpy (4,4’-di(5-nonxyl)-2,2’-bipyridine) as the ligand and they demonstrated that the addition of surfactant (SDS) increased the efficiency of the polymerization by increasing molecular weight and polydispersity [98]. The interaction between copper (II) bromide or chloride with sulfate anions decreased the probability of termination, is to deactivation of growing radicals. Furthermore, nonionic surfactants (Brij 97 and Brij 98) were applied into the polymerization. Even though the related polymer was obtained in case of these surfactants, in the Brij 97 colloidal stability was not observed because of coagulation. In addition, the emulsion polymerization

was effectively provided for styrene, butyl acrylate and methyl methacrylate. Considering the differences between bulk and emulsion polymerization of these monomers, n- BMA did not showed any different behaviors in the mentioned polymerization types, but styrene and butyl acrylate showed different rates in the two-polymerization methods. The slower rates were found in bulk polymerization. Additionally, it was resulted that copper (II) halides complexed with water-soluble ligands caused uncontrolled polymerization. In this study, the well-controlled polymerizations provided that the molecular weights were almost same with theoretical values and the polydispersities were found in the range of 1.2-1.3.

Although, ATRP is performed by a monomer-soluble initiator such as EBib (ethyl 2-bromoisobutyrate), reverse ATRP can be carried on with a water-soluble initiator that it makes describing of the polymerization more clear with respect to traditional emulsion polymerization. According to the schematic representation of the mechanism of reverse ATRP in Figure 2.9, the most common initiator is converted to radicals, whose high oxidation species react with a ligand. The efficient ability of the radicals included the complex particle to decompose in a rapid way provides that all polymer chains are initiated. As an illustration, Qiu et al demonstrated controlled emulsion polymerization with the ATRP of the BMA in the presence of various water-soluble initiators (KPS, V-50, V-044) and Cu(II)dibromide as a catalyst with 4.4'-dialkly-2,2'-bipyride ligands [100].

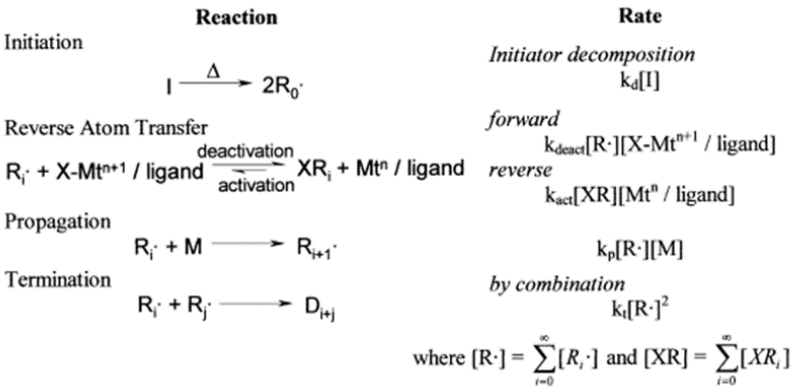


Figure 2.9 : Reverse ATRP mechanism.

As compared to the emulsion based on initiators, azo compounds (V-50, V-044) were more profitable for the reverse emulsion ATRP of n-BMA. Since, the initiators resulted in well-controlled polymerization in spite of the absence of buffer solution and lower initiation efficiencies that reflected by 2-3 times more molecular weights,

especially in the presence of V-50. The distribution of molecular weight can be seen in Figure 2.10. It was determined that the lower value resulted from decreasing radicals in the aqueous phase by $CuBr_2$ without complex. It was also observed that how to change molecular weight with regard to the ratio of $CuBr_2$/V-50 and the dependency could be seen in Figure 2.11. Furthermore, the KSN provided the polymerization with only the usage of a buffer; also, the obtained latex was stable in this process. Additionally, in this study it was seen that the azo compounds were responsible for bigger particle sizes (< 300nm) than the KPS (>2μm).

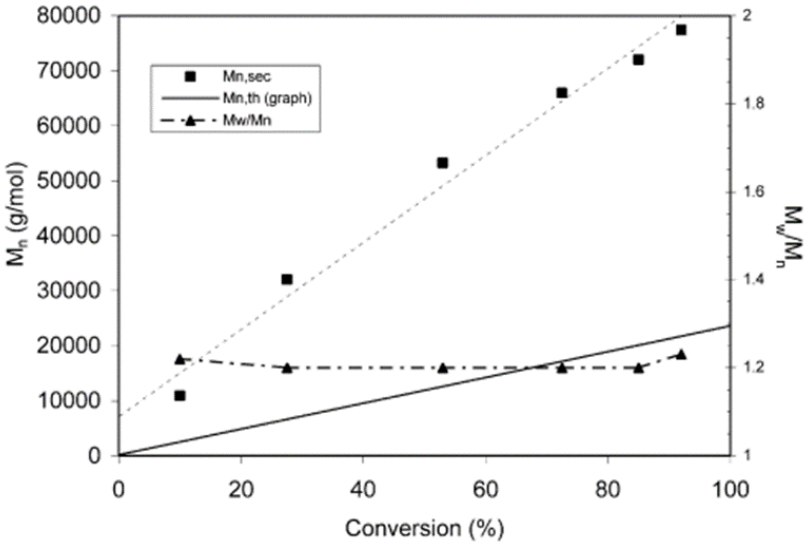


Figure 2.10 : Mn and PDI dependence on conversion for emulsion by reverse ATRP (V-50 initiator) [100].

To investigate the mechanism of the ATRP reverse emulsion of n-BMA/water mixtures in a detail way, the researchers continued studies with regarding the act of a surfactant (Brij 98) and the partitioning of a catalyst (copper complexes mentioned in the previous study).

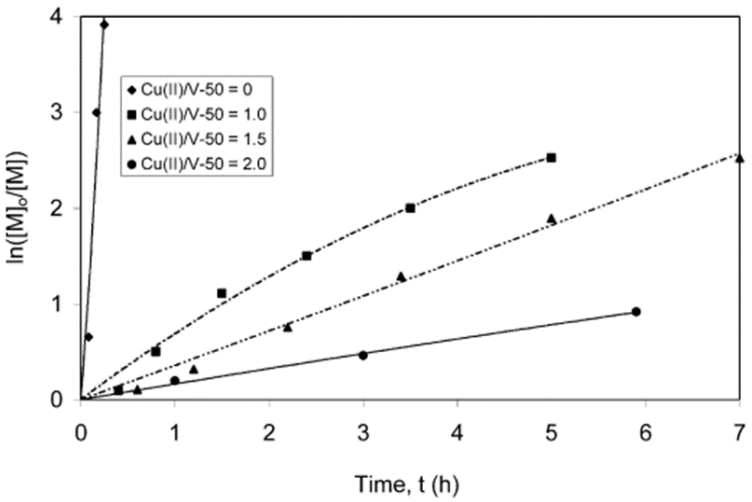


Figure 2.11 : Emulsion polymerization kinetic of ATRP with $CuBr_2$ [100].

The copper complexes were found as Cu (II) and Cu (I) complexes. The Cu (II) complexes dissociated to form Cu (II) and free ligand in the organic phase and the Cu (I) complexes showed the higher ability of the solubility in organic phase. Here in, at 900C, 20-30% of Cu (I) was observed in the aqueous phase in case of sufficient transfer rates through the aqueous phase. Moreover, they mentioned that the Cu (II)/ligand complexes, free excess ligand and some surfactant were found in the monomer droplets, while dissolved monomer, micelles, initiator, surfactant and small amount of the Cu (II)/ligand complexes were found in the aqueous phase [101]. In this study, the effect of some parameters on the reverse ATRP were determined. Especially, these parameters were temperature, the ratio of catalyst/ligand to initiator ($CuBr_2$/dNbpy to V-50), and initiator (V-50) concentration. Regarding the effect of temperature, an increase results in enhancing initiator efficiency due to lower primary radical flux. Thus, the period of imitation of all chain extents, subsequently the wide of molecular weight could be observed. On the other hand, a decrease in the temperature causes higher termination early in the polymerization, reflected with fewer chains. Therefore, the decline results in higher molecular weights and lower polydispersities [101]. Moreover, the ratio of catalyst/ligand ($CuBr_2$/dNbpy) to initiator affects the length of induction period, which can be described with the conversion of Cu (II) to Cu (I) radicals transferred from the aqueous phase to the organic phase, mostly micelles in order to be deactivate inside oligomers. The period also reflects reaction rate, since it changes with the ability of Cu (II) initially entered in the organic phase to form oligomeric radicals. It means that if the amount of Cu (II) is not enough to react with oligomers inside micelles, some Cu (II) in the

aqueous phase would transfer to organic phase. That is to say, lower induction times result in higher conversion rates. Finally, when the initiator concentration increases in the emulsion, the reaction rate decreases, resulting from lower the number of expected chain and increasing the deactivating of Cu (II) concentration.

2.4.2 RAFT in emulsion polymerization

According to many studies, reversible addition-fragmentation transfer in emulsion can be applied successfully to a great number of monomer under different conditions. However, the effect of the transfer agent on polymerization is still required to check because of heterogeneity of the emulsion system. In order to indicate the effect, Monteiro et. al studied with seeded styrene emulsion polymerization [25]. They determined that the polymerization might not occur based on zero- one kinetics, which can be seen in the conventional polymerization. Since, they are responsible for the different way of termination. The common polymerization, in which an oligoradical enters into a particle as one growing radical into the particle that represents the termination between short and long radicals in an instantaneous way, while in the polymerization with RAFT agent the oligoradical may give its activity long radical before it transfers inside the particle that means the termination between two long radicals is not shown instantaneously. Also, they indicated that the type of RAFT agents, presenting their leaving groups affected on rate retardation and polydispersities, when there was seeded styrene emulsion polymerization with dithiobenzoates ($C(CH_3)_2Ph$ and $C(CH_3)_2CO_2Et$), which differed from each other based on the leaving groups of different water solubilities. They showed that their greater activities and the ability to insoluble in water caused that they need to overcome potential transfer limitations on diffusion [25].

Furthermore, Monteiro and de Barbeyrac investigated that how exit and re-entry of 1-(O-ethylxanthyl) ethylbenzene as a RAFT agent in styrene emulsion polymerization affects final particle size and reaction rate [102]. They stated that the concentration of the RAFT agent was lower than the overall bulk value, so it was suggested that the RAFT agent could be partitioning at the particle interface. By considering the outcome, they would produce core-shell block copolymers which polystyrene occured in the cores and the shells consisted of poly (n-butyl acrylate-co-acetoacetoxyethyl) [102].

In addition, Charmot et. al demonstrated that the usage of MADIX in ab inito emulsion polymerization of styrene and butyl acrylate resulted in higher polydispersities than high activity RAFT agents [103]. Therefore, it was concluded that semi-batch operation was more profitable to form 100% dormant chains in the early time of polymerization. Then, Monterio proved that the semi-batch operation provided the formation of purer blocks in the polymerization of styrene and butyl acrylate with the MADIX [104]. However, internal mass transfer limitation are still required to check with much smaller catalyst size (< 70 μm carbon size) and higher metal loading on same carbon size in order to see the utilization of carbon supported Pt catalysts in APR in a detail way. However, porous carbon materials may suffer from mass transfer resistance based on their structural morphology (especially, pore size). The relevant effect of mass transfer resistance is seen as the limitation of activity and selectivity.

2.4.3 NMRP in emulsion polymerization

Stable free radical polymerization, which is identified as a nitroxide-mediated radical polymerization, includes three main steps based on the transfer of nitroxide to monomer droplets, aqueous phase and micelles, respectively. Particularly, nitroxide constitutes radicals of the monomers, representing the oxide transfer from the droplets to the aqueous phase at first. Then, the formation continues until the grown of the radicals is enough to enter the micelle or the particle. The radicals can also stay in the aqueous phase by the interaction with the nitroxide. Finally, the oligoradical inside micelle react with nitroxide or another radical to obtain deactivated form [49].

This kind of polymerization is bound up with the thermodynamically balance of the nitroxide among the three phases; droplets, particles, aqueous phase. That is to say, the polymerization can control with the partition coefficient of the nitroxide between phases and aqueous phase diffusivity of the oxide. Although, the aqueous phase diffusivity reaches the equilibrium point easily, the balancing of the partition coefficient is hard due to the different concentration of free nitroxide and loss of a portion of the nitroxide into the aqueous phase from particles. Providing that free nitroxide does not interact with an expanding macroradical chain to deactivate the chain, it may maintain stable in particle. On the other hand, the nitroxide can appear

in the aqueous phase if the chain gains activation. The aqueous nitroxide can form a short radical oligomer with the water-solubility of monomer. The growth of the oligomer depends on the concentration of monomer in the water-rich phase: if the concentration is high, the growth carries on until the chain is insoluble, then penetrate into a particle. Whereas, the concentration is low, the growth is not enough that the chain enters a particle; also, the oligomer radicals may undergo irreversible termination with other radicals. It means that the oligomer radicals cannot combine with each other to form an insoluble chain, which is responsible for the transfer into particle [49].

Heterogeneous NMRP reactions in emulsion have been adopted in different studies, especially considering styrene polymerization in presence of nitroxides. Bon et al. demonstrated that almost complete conversion was achievable for seeded styrene polymerization performed with alkoxyamine at 125^0C during 36 hours [44]. The high conversion was linked with lower molecular weights, which resulted from bimolecular termination and additional radical formation driving force system heterogeneity effects and enhanced Diels-Alder reaction, respectively. They also indicated that the lower weights obtained in the study than theoretical weights resulted in seed polymer along with nitroxide-meditated polymer. Additionally, they showed that instability of bimolecular termination at extended reaction time caused widening in distribution molecular weights [44].

Observing an the first ab initio nitroxide-mediated styrene polymerization, Marestin et al. evidenced that it was compelling to adjust conditions for a stable latex with high conversions, because the known surfactants were destroyed under long polymerization time and high temperatures [45]. To solve this, they used KPS as initiator and SDS as surfactant at 130 ^{0}C in the presence of hexadeconal, then, they provided increase in the latex stability; however, the process acted as a miniemulsioın polymerization. Therefore, their studies were directed to several nitroxides. The most attractive outcome was reported as 69% conversion with a polydispersity of 1.7 at 36 hours in the presence of 4-amino-2,2,6,6-tetramethyl-1-piperidinxyloxy (4-amino- TEMPO). In addition, an amino alkoxyamine gave the same conversion reflected same polydispersity value (1.7), but it ensured a higher molecular weight. It could be concluded that they provided higher polydispersity than typically values of bulk NMRP polymerization [45].

Regarding to attain well-controlled reactions in styrene emulsion polymerization, Cao et al studied with four differently substituted TEMPO derivatives, which were found in different water-solubility [47]. The study showed that a decrease in the solubility caused an increase polymerization rate. The most interesting results were observed as 81% conversion, molecular weight of 18 000 and polydispersity of approximately 1.3 by using 4-acetoxy-2,2,6,6-tetramethyl-1-piperidnyyloxy (ATEMPO), also the late was stable and the proper particle size was ‹100 nm. It was notably that the portion of higher molecular weight was more dominant at low conversions due to some particles being nucleated with other particles instead of nitroxide [47].

Herewith, it can be stated that NMRP emulsion polymerization should overcome colloidal instability to be efficient polymerization system. To indicate characteristics of nitroxide partitioning, Ma et al measured the most common nitroxides, TEMPO, 4-amino-TEMPO and 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy in styrene-water systems at temperatures between 25 to 135 ^{0}C [105]. Particularly, TEMPO showed higher solubility in styrene, while 4-amino-TEMPO and 4-hydroxy-TEMPO were more soluble in water. It was also observed that the addition of hexadecane, surfactant and polystyrene were negligible.

2.4.4 ATRP in miniemulsion polymerization

ATRP technique is adapted to the aqueous media polymerization (emulsion, mini/microemulsion) as well as other CLRP systems. However, in literature ATRP adapted miniemulsion polymerization systems were performed in the presence of copper complexes as catalyst. The success of ATRP technique in the water environment depends on the high solubility of the copper complexes in the monomer phase. Beside this, the choice of both the ligand and the surfactant is also important. Bipyridines or other hydrophobic ligands should be preferred for an effective miniemulsion process. The surfactant should not interact with the catalyst in reaction medium. For this reason, it has been reported that nonionic and cationic surfactants are effective in ATRP adapted miniemulsion systems [50, 106].

ATRP technique can be carried out in three ways including direct ATRP, AGET-ATRP and reverse ATRP. While direct ATRP is the most commonly known and

applied method, other approaches have been preferred in which the oxidation sensitivity of Cu (I) complexes during emulsification is prevented [50].

N-butylmethacrylate polymerization was carried out in a successful miniemulsion operation by direct ATRP method [99]. Brij 98 was preferred as non-ionic surfactant and CuBr/dNbpy was used as the catalyst. With good control in the reaction, high yields (about 70%) were achieved in short reaction time and polymer particles were obtained with low PDI values and about 300 nm avarage particle size [99].

The use of conventional water-soluble initiators and the inhibition of Cu oxidation provide a significant advantage in the preferred reverse ATRP method instead of direct ATRP. With these advantages, the induction period is observed in this method depending on the polymerization temperature, deactivation/initiator ratio and Cu (II) concentration. In the same study [99], nBMA polymerization was also carried out by reverse ATRP method comparing with direct ATRP method. Cu (II) was used instead of CuBr copper complex and Brij 98 was preferred as surfactant. It has been observed that the water-soluble initiator provides better control over the molecular weight with high initiator yield as compared to the oil-soluble initiator. There was no difference in colloidal structure during the reaction between two systems.

In another study, nBMA polymerization was carried out in the presence of VA-060 initiator and Brij 98 surfactant, in which the ligand was highly active. In this study, the amount of surfactant needed was reduced through the activation of ligand and optimum conditions, good control and livingness were achieved at lower temperature (70^{o}C). When the surfactant concentration is high, the hydrophobic ligand needs to be at a higher level so that control and livingness are lost in the reaction medium. In this case, both the droplet and the micellar nucleation occur together. The amount of surfactant required can also be adjusted by the hydrophobicity of the ligand [107].

In another study, the nBMA polymerization was carried out using a cationic surfactant, CTAB, by reverse atrp method. In this study, as monomer conversion increased, linear increase in molecular weight and decrease in PDI values were observed. The stability of the miniemulsion in the reaction medium can be provided by lower surfactant concentration (1%, by weight to monomer) [108]. At lower temperatures, high molecular weight (106 g.mol-1) and low PDI values were

achieved in the polymerization using the ascorbic acid/hydrogen peroxide redox initiator system.

AGET-ATRP is also a useful technique for miniemulsion conditions such as reverse ATRP. The methacrylate and styrene polymerizations were carried out with copper complex and ascorbic acid agent in the presence of the appropriate ligands. The ascorbic acid in the medium consumes oxygen. In this way, the Cu (II) complex is also reduced and the reaction proceeds in the presence of air. In this way, the deoxidation step is eliminated. This is an important feature of AGET ATRP [109, 110].

Minimemulsion polymerization of styrene and butylacrylate was carried out by AGET-ATRP method. In this study, a block copolymer of polyethylene glycol and polystyrene is used as stabilizer and initiator. Reaction was performed without surfactant. Low PDI values and highly efficient control/livingness were obtained with polymer particles of 150-200 nm size [111].

AGET-ATRP method is also a useful technique in the production of hybrid materials. In a study, butyl acrylate polymerization was carried out by using functionalized silica as a macroinitiator, in miniemulsion medium with AGET ATRP technique and hybrid materials could be obtained with higher yields than bulk polymerization. At the same time, the gelation observed in the hybrid materials resulting from bulk polymerization has not been observed in the products obtained by AGET-ATRP adapted miniemulsion polymerization [112].

It can be said that the inverse miniemulsion polymerization can also be adapted to AGET-ATRP. Inverse miniemulsion polymerization is generally suitable for water-soluble polymers. This method was used in the polymerization of polyethyleneglycol methyl ether methacrylate monomer. By well-controlled reaction, products with low PDI values and ~200 nm in size, were obtained [113].

2.4.5 RAFT in miniemulsion polymerization

RAFT polymerization is a CLRP technique, which can be carried out with a most variety of monomers and provides desired molecular architecture. In emulsion systems, RAFT polymerization has been of particular interest. However, in literature a few problems such as high levels of coagulum, very slow polymerization rates, thick red layers depends on phase separation and loss of molecular weight control

have been reported in RAFT emulsion systems [21-25]. Recently, a lot of works focused on the applications of RAFT polymerization in miniemulsion and microemulsion systems in order to prevent these problems [26-29]. Liu et al. studied RAFT polymerization of n-hexyl methacrylate for the first time in microemulsion and compared the results with those of conventional microemulsion polymerization. They reported that RAFT technique could be successfully used in microemulsion system and more stable latex particles even in the range of 18-30 nm size could be obtained [28]. Additionally, there are a number of successfully completed studies on the RAFT mediated aqueous media polymerization of styrene [26, 30, 31], methyl metacrylate [27, 32], vinyl acetate [33] and fluoroacrylates [29].

Huang et al. studied RAFT polymerization in miniemulsion condition by using SDS and hexadecane as surfactant and cosurfactant, respectively. They performed styrene polymerization in the presence of CDB as a RAFT agent in their study. Ostwald ripening effect caused instability with large size droplets and phase separation was observed. When polymerization carried out in different loci bimodal size distribution was observed [114].

If RAFT polymerization is not carried out under suitable miniemulsion conditions, formation of color layer, low reaction rate and formation of coagulation are observed. It is still unclear why this coagulation arise. Luo et al. claim that this colloidal irregularity originates from the ‘’superswelling’’ effect. With this effect droplet nucleation is interrupted. According to this disclosure, nucleation of uncharged monomer droplets results in diffusion into the polymerization environment, thereby increasing the oligomer concentration with low molecular weight in reaction medium. This causes colloidal instability by lowering RAFT yield [115].

In RAFT mediated miniemulsion system, surfactant type is of great importance for achieving colloidal stability. Several studies were performed by using ionic and nonionic surfactants. In these studies, this stability problem was observed in styrene, butyl methacrylate and methyl methacrylate polymerizations. The instability, which is seen when using ionic surfactant, is not observed when nonionic surfactant is used and a more controlled reaction environment is provided. In both cases retardation occurred [23, 116].

2.4.6 NMRP in miniemulsion polymerization

Recently, NMRP mediated polymerization systems are used in heterogeneous systems, especially emulsion polymerization. In emulsion polymerization, NMRP systems show several problems such as colloidal instability and low latex conversion. Some studies reported that high reaction yields (~70%) were achieved by using different nitroxide radicals such as 4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy and amino alkoxyamine [44-47]. It is thought that colloidal instability in NMRP mediated emulsion polymerization is due to the nucleation step and polymerization in droplets as an additional polymerization loci. Conventional emulsion polymerization takes place in particles and the polymerization rate is higher in particles comparing to monomer droplets. Monomer droplets act as a monomer reservoir. However, NMRP mediated emulsion system, droplet nucleation can not be negleted because of the same level polymerization rate in particles and droplets [47]. NMRP adapted miniemulsion system is evaluated in two parts due to the behaviour of initiating system. These are bicomponent system and monocomponent systems [50]. These systems can be also classified according to the kinds and solubilities of the initiator: water-soluble and oil-soluble. NMRP adapted miniemulsion polymerization includes different types of initiating system such as bicomponent and alkoxyamine system with oil/water soluble initiators [50]. As it is known, in miniemulsion polymerization monomer droplets act as a nanoreactor. In this way, bicomponent system with oil soluble initiator is quitely effective for miniemulsion process. Prodpran et al. reported a succesful NMRP adapted miniemulsion polymerization of styrene by using TEMPO radical, benzoil peroxide (BPO), as an oil soluble initiator, and Doxfax 9380 as surfactant with bicomponent initiating system [51]. Furthermore, when a water-soluble initiator was used in the same system, TEMPO/KPS ratio was reported to be important and high monomer conversion and low PDI values were obtained with optimized TEMPO/KPS initial ratio [52].

Cunningham and co-workers studied styrene polymerization by NMRP adapted miniemulsion system. They used TEMPO and TEMPO-OH as nitroxide radical in their system with sodium dodecylbenzylsulfate (SDBS) and investigated kinetic effects of camphorsulfonic acid (CSA) on miniemulsion system. They finally noted that addition of CSA provides an improvement effect on the rate of polymerization.

Nevertheless, products obtained in the presence of CSA had higher molecular weights Reaction kinetics was not depend on the type of nitroxide radical but reactions carried out in the presence of TEMPO had better control than reactions with TEMPO-OH [117]. In another study, SG1 have been used as nitroxide radical in miniemulsion polymerization and styrene could be successfully polymerized by using AIBN, as an oil soluble initiator. Although molecular weight distribution values have acceptable, monomer conversion was limited about % 60 in 24 h due to the free nitroxide radical in the reaction medium [118]. In another study, nitroxide mediated miniemulsion polymerization was performed with redox initiating system, KPS/sodium metabisulfite, by using SG1 as a nitroxide radical and polymerization rate was enhanced compared to AIBN initiated system. The optimum ratio of SG1/KPS was determined. PDI values were found acceptable [119]. Monocomponent initiator system provides higher initiating efficiency than bicomponent system. These systems include oil soluble and water soluble alkoxyamine initiators such as PS-TEMPO, PS-TEMPO-OH, BST-TEMPO, MONAMS and BlockBuilder [50]. PS-TEMPO which is nitroxide terminated radical was used for the production of styrene with Dowfax 8390 and hexadecane as surfactant and cosurfactant, respectively. Molecular weight distribution of products obtained by PS-TEMPO monocomponent initiating system was found nearly 1.8 and polymerization yield reached to 70 % after 12 hours [120].

In recent years, controlled/living radical polymerization techniques have been applied for various purposes under emulsion and mini/microemulsion conditions. Liu and co-workers prepared graphene oxide based cadmium imprinted polymer (Cd (II)-IIP) by RAFT polymerization in microemulsion condition. They used the RAFT method to provide the functionality and molecular architecture of the imprinted polymer. The microemulsion medium was preferred for providing a stable polymerization process in their study. The product obtained with good uniformity showed thermal stability and high adsorbtion performance [121]. Peralta et al., studied vinylacetate polymerization in both conventional and controlled miniemulsion processes. For the first time, they used gamma ray as a source of initiator in this study. They performed polymerization in controlled way by using the RAFT/MADIX method. They observed that better molecular weight distribution was achieved in the controlled miniemulsion compared to conventional miniemulsion

polymerization. It was found that the gamma ray in the RAFT-adapted miniemulsion system was better than the classical initiators such as AIBN and high conversions were observed in short time [122]. Zetterlund and co-workers studied styrene/divinyl benzene polymerization with inverse minemulsion polymerization by using the RAFT technique. Toluene and n-hexane mixtures were used as continuous phase in the inverse miniemulsion. Poor colloidal stability was observed in the continuous phase prepared with the 50:50 ratio of toluene:n-hexane. The obtained polymer nanocapsules had average particle diameters about 300 nm. The particle size distribution was better in the polymerization carried out in pure toluene. The increasing amount of n-hexane degrades the droplet stability in the polymerization [123]. Zhou and co-workers studied ab initio RAFT polymerization of fluorinated polyacrylate by emulsifier-free emulsion polymerization. They used a macro RAFT agent (PDMAEMA-b-PHFBA). Products with low molecular weight distribution were obtained in the context of controlled polymerization. By means of TEM analyzes, spherical particles were observed in the range of 40-60 nm. As a result of GPC analysis, it was observed that the polymers were obtained with low PDI value as 1.40 [124]. Okubo et al. prepared polymeric microcapsules with encapsulated HD as a heat storage material. Polymerization was performed with AGET-ATRP technique by using microsuspension activators. They produced polar poly (ethylene glycol dimethacrylate) (PEGDM) particles encapsulated HD and these materials showed excellent heat storage properties [125]. Zhu and co-workers prepared polyacrylate with reverse ATRP mediated emulsion polymerization. They used an electrolysis technique to remove residual copper from latexes. The reaction was performed by a new surfactant-ligand system by using $CuCl_2$/4,4-di-(5-nonyl)-2,2′-bipyridine (dNbpy) as ligand and Brij-98 as surfactant. This alternative system provided the capture Cu species residing at the interface of latex particles and colloidal stability was achieved [126].

3. EXPERIMENTAL PART

3.1 Materials and Chemicals

Styrene (St, 99%, Aldrich) was passed through a basic alumina column to remove the inhibitor. Commercially purchased linseed oil was used as the oil component after air-blowing process. Methanol (≥99.8%, Sigma-Aldrich), ethanol (≥99.5%, Sigma-Aldrich), diethyl ether (≥99%, Sigma-Aldrich), carbon disulfide (99.5%, Merck), toluene (≥99.8%, Sigma-Aldrich), glycerol (≥99.5%, Merck), sulfuric acid (95-98%, Merck), pyridine (≥99.8%, Sigma-Aldrich), potassium hydroxide (≥85%, pellets, Sigma-Aldrich), benzene (anhydrous, ≥99.8%, Sigma-Aldrich) and tetrahydrofuran (THF, (≥99.9%, HPLC grade, Sigma-Aldrich) were used as received. 2,2 Azobis(isobutyronitrile) (AIBN, 98%, Sigma-Aldrich) was re-crystallized twice from methanol. Cetyl trimethylammonium bromide (CTAB, surfactant, from Sigma-Aldrich), DOWFAX 8390 (surfactant, from Sigma-Aldrich), and hexadecane (HD, co-stabilizer, Sigma-Aldrich) were used without further purification. Phenacyl morpholine dithiocarbamate (PMDC, Raft agent) was synthesized and purified according to the literature. 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (99%, Sigma-Aldrich) was used as recieved. 4,4'-Azobis(4-cyanopentanoic acid) (ACPA) (≥75%, Sigma-Aldrich) and thionyl chloride (≥99.0%, Sigma-Aldrich) was used as recieved for synthesis of 4,4'-Azobis(4-cyanopentanoic chloride) (ACPC). Dichloromethane (anhydrous, ≥ 99.8%, Sigma-Aldrich) was used as reaction medium for ACPC synthesis. 1,4-dioxane (anhydrous, ≥99.8%, Sigma-Aldrich) and xylene (anhydrous, ≥ 99.8%, Sigma-Aldrich) were used as reaction medium for solution polymerization reactions. Lead naphtanathe (0.5%) and cobalt naphthenate (0.05%) was used as drier for film applications.

3.2 Characterization and Equipment

3.2.1 Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy

^{1}H-NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard for structure analysis.

3.2.2 Fourier-transform infrared (FT-IR) spectroscopy

The Fourier-Transform infrared spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer for structure analysis.

3.2.3 Dynamic light scattering (DLS) analysis

The droplet and particle size distributions for copolymer samples were monitored by dynamic light scattering (DLS, Zetasizer 4000, Malvern) system.

3.2.4 Gel permeation chromatography (GPC) analysis

The molecular weight and molecular weight distributions of the resulting polymers were determined by gel permeation chromatography (GPC) employing an Agilent 1100 instrument equipped with a differential refractometer by using tetrahydrofuran (THF) as the eluent at a with molecular weight ranging from 580 to 355,000 g mol^{-1}.

3.3 Preparation Methods

3.3.1 Preparation of air-blown linseed oil

Air blowing process was carried out by air passing through linseed oil with a constant flow rate (2L/min) for 18 h at 80 $^{\circ}$C in a temperature-controlled system. The peroxide values of air-blown linseed oils thus obtained were determined according to the literature [127].

3.3.2 Synthesis of phenacyl morpholine dithiocarbamate (PMDC)

PMDC (RAFT agent) was prepared according to the method which is described in literature [85].

3.3.3 Synthesis of styrenated oil by RAFT-mediated miniemulsion polymerization

Miniemulsion was prepared according to the following procedure: Monomers (air-blown linseed oil:styrene, 1:1, by weight) were mixed with a given amount of hexadecane and PMDC to form organic phase. AIBN, as an oil soluble initiator, was added to this organic phase and stirred with magnetic stirrer for 20 min. This mixture was then slowly added to the separately prepared solution of CTAB in de-ionized water under stirring for 20 min. The mixture was ultrasonified by using an ultrasonifier (Bandelin SONOPLUS HD 3200, amplitude 70%, 400 W) for a time period of 15 min. The obtained miniemulsion was transferred to a 250 ml three-neck flask, equipped with a condenser, thermometer and then deoxygenated by purging with nitrogen for 10 min. Then the flask was placed in an oil bath at 70◦C and after the required duration, the reaction was quenched by cooling the flask. The polymer product was precipitated in methanol, washed with methanol and dried at 30◦C under vacuum for 24 h. The polymerization yields were determined gravimetrically. The styrenated oil samples were also prepared by classical RAFT polymerization in solvent (dioxane) in order to compare the results with those of the samples of this study under miniemulsion conditions.

3.3.4 Synthesis of partial glycerides of linseed oil

Partial glycerides were obtained by glycerolysis reaction between triglyceride oil and glycerol. Linseed oil (200 g) and glycerol (17 g) were placed in a three necked reaction flask and heated. When the temperature reached to 218 ^{o}C, 0.2 g calcium hydroxide (0.1%, by weight to oil portion) was added to the mixture as catalyst. After the catalyst addition, nitrogen was passed through the reactor for 5 min. When the temperature reached to 230^{o}C, the reaction was continued for 1 h at this temperature. Samples taken from the reaction mixture were added to ethanol (x3 amount of sample) and when the ethanol phase became clear, reaction was terminated. Then glycerolysis product was cooled and dissolved in diethyl ether. The mixture was placed in a separatory funnel and washed with sulfuric acid (0.2 N) to remove catalyst and then washed with distilled water to remove sulfiric acid and free glycerol. The solution was dried overnight with anhydrous Na_2SO_4. Finally, diethyl

ether was removed by rotary evaporator and then hydroxyl and acid values of product were determined by related procedures [127].

3.3.5 Determination of hydroxyl and acid values of partial glycerides

Hydroxyl value determination of partial glycerides was performed in three tests including two oil samples and one blind test. Oil samples (1 gr for each flask) was placed into two flasks. Third test flask without sample was prepared for blind test. 5 ml acetylating agent (acetic anhydride:pyridine, 1:3 by volume) was added into flasks. Flasks were poured into a preheated oil bath at 104^{o}C. After one hour, samples were cooled and then 2 ml distilled water was added into all flasks. Samples were incubated for 10 min more in oil bath at 104^{o}C and titrated with alcoholic KOH in the presence of thymol blue indicator after cooling. Titration was performed until yellowish color turns into blue and expended amount of KOH was determined by volume for two oil and one blind tests. Expended KOH volume for oil sample was determined as the average of two tests and hydroxyl value of partial glycerides was calculated by the equation 3.1.

$$\text{Hydroxyl value} = \frac{(\text{Vblank} - \text{Vsample})\text{x}56.1\text{xN}}{\text{amount of sample (g)}} + \text{acid value} \qquad (3.1)$$

$N : Normality\ of\ KOH\ solution.$
$Vblank : Expended\ KOH\ volume\ for\ blind\ test.$
$Vsample : Average\ expended\ KOH\ volume\ for\ two\ oil\ tests.$

Two tests were perfomed to determine the acid value of prepared partial glycerides and then the average of these tests was used as acid value for hydroxyl value determination represented by the equation 3.1. For acid value determination, 1 gram of sample was weighed for each tests and then 5 ml ethyl alcohol and 5 ml toluene were added into the flasks. Oil samples were dissolved with magnetic stirring and then titrated with alcoholic KOH in the presence of phenolphthalein indicator. Titration was performed until transparency turns to violet color for each test. Expended KOH volumes were determined and the average value of these tests was used in equation 3.2 for acid value determination.

$$\text{Acid value} = \frac{56.1\text{xVxN}}{\text{amount of sample (g)}} \quad (3.2)$$

$N : Normality\ of\ KOH\ solution.$

$V : Average\ expended\ KOH\ volume\ for\ two\ oil\ tests.$

3.3.6 Synthesis of 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC)

4,4'-azobis(4-cyanopentanoic acid) (ACPA) was dispersed in 150 ml dichloromethane (DCM) and stirred for about 1 h at room temperature. After stirring, the mixture was cooled and thionyl chloride was gradually added by dropping funnel at 0^{o}C. After the adding thionyl chloride within 20 min, reaction mixture was stirred for 12 h at 35 ^{o}C. Solvent (DCM) was evaporated by rotary-evaporator and 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC) was obtained as yellow solid powder. The product was washed with DCM and precipitated in hexane for removing unreacted thionyl chloride. ACPC separated from the liquid phase was dried at room temperature under vacuum for 24 h [128].

3.3.7 Synthesis of linseed oil based macroinitiator (OBMI)

A certain amount of ACPC in dichloromethane was added dropwise to a mixture of the equivalent amount of partial glycerides in pyridine at 0 $^{\circ}$C. After 30 min, the temperature was raised to 35 $^{\circ}$C and kept constant while stirring for 80 h. The reaction mixture was then dissolved in diethyl ether, washed with 0.1% aqueous sulphuric acid solution and water, and finally dried over Na_2SO_4. After removing the solvent, oil-based macroinitiator was characterized by FT-IR and ^{1}H-NMR analysis.

3.3.8 Synthesis of styrenated oil by NMRP-miniemulsion polymerization

Miniemulsion was prepared according to the following procedure: 0.2 g ($1.5x10^{-4}$ mol) OBMI and 1 g styrene ($9.6x10^{-3}$ mol) were mixed with a given amount of HD (4 %, by weight of styrene) and TEMPO ($1.5x10^{-4}$ mol) to form organic phase and stirred with magnetic stirrer for 20 min. This mixture was then slowly added to the separately prepared 50 ml aqueous solution of DOWFAX 8390 and stirred for 20 min. The mixture was ultrasonified by using an ultrasonifier (Bandelin SONOPLUS HD 3200, amplitude 70%, 400 W) for 15 min. The obtained miniemulsion was deoxygenated by purging with nitrogen for 10 min and transferred to the reactor. The temperature was set to 125 ^{o}C and after the required durations, samples were taken

from reaction medium. The polymer product was precipitated twice in tenfold methanol and dried at 30 ^{o}C under vacuum for 24 h. The polymerization yields were determined gravimetrically. The styrenated oil samples were also prepared by classical NMRP polymerization in solvent (xylene) in order to compare the results with those of the samples of this study under miniemulsion conditions.

3.3.9 Determination of film properties

Film properties of styrenated oil samples obtained by miniemulsion were determined. Film properties such as drying time [129], flexibility [130], adhesion [131], water resistance [132], alkali resistance [132], and acid resistance [132] were applied according to standard test methods. For each test method, sample was thinned with xylene to 30% solid content, and 0.5 % lead naphthenate and 0.05 % cobalt naphthenate as metal based on solid content were added. Film coating was applied 24 h after addition driers. For drying time test, polymer films (60 μm) were prepared on glass surfaces by using a film applicator. The flexibility, water resistance and adhesion tests were applied by using tin plate panels as a substrate. For alkali and acid resistance tests, dipping method was employed by using glass tubes as explained in the related standards.

4. RESULTS AND DISCUSSION

4.1 Styrenation of Air Blown Linseed Oil via RAFT –mediated Miniemulsion Polymerization

Controlled/living radical polymerization techniques could be successfully applied for styrenation of triglycerides [13-16]. In the first part of this thesis, RAFT polymerization was performed in miniemulsion medium and styrenated oil samples with low PDI could be obtained under the applied conditions. The overall process and the representative structures of the obtained styrenated oil are explained in Figure 4.1.

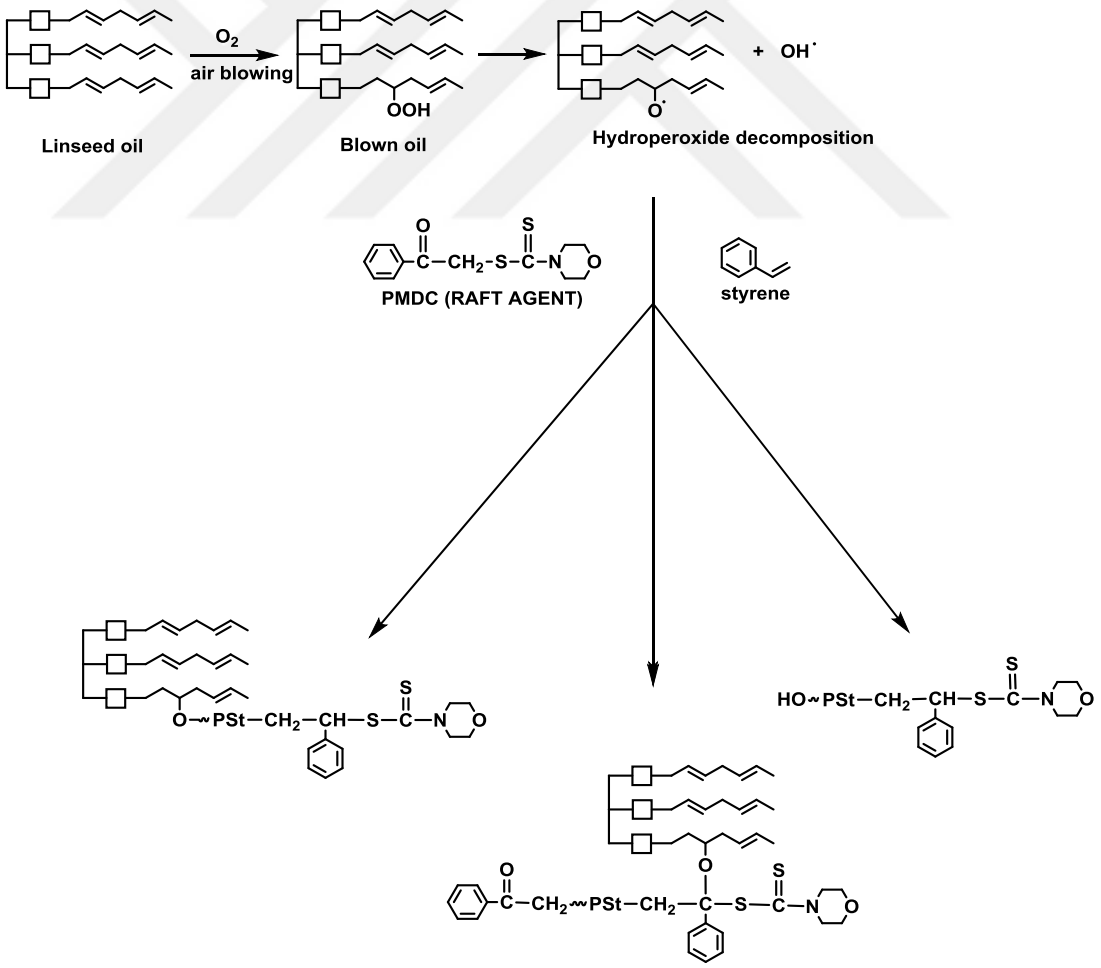


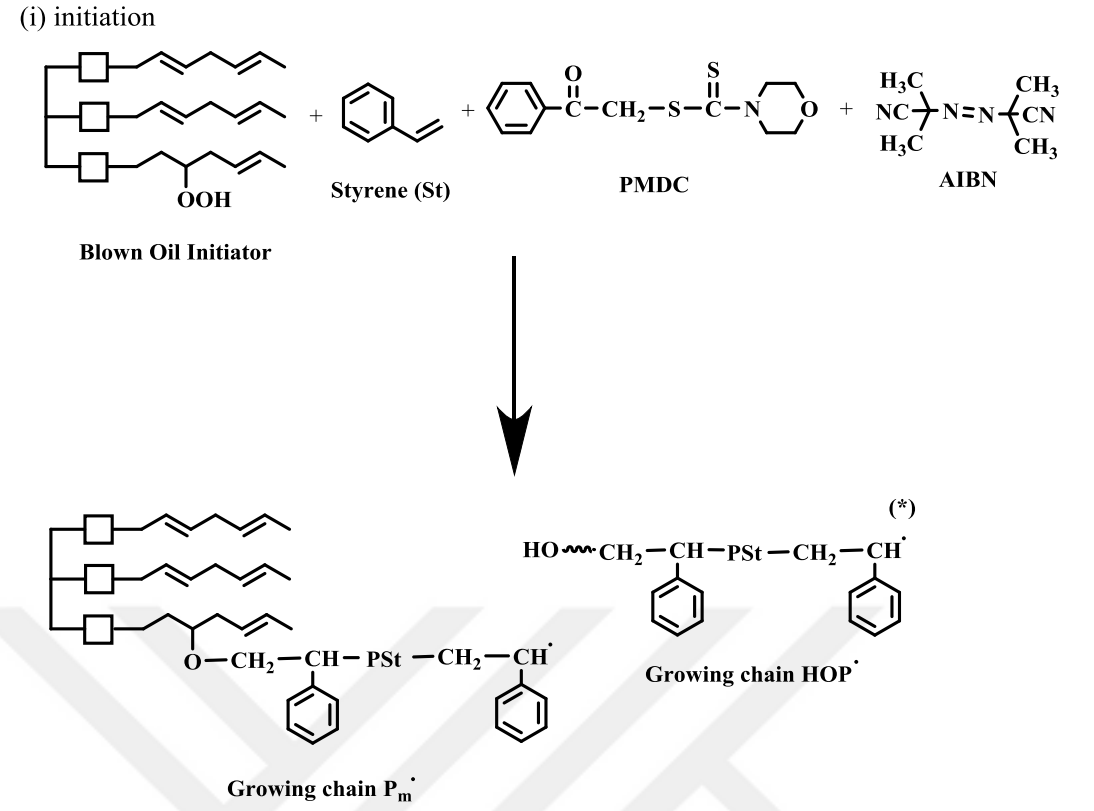
Figure 4.1 : Representative styrenated oil structure obtained by RAFT polymerization technique.

As seen in Figure 4.1, the first step of the process is the ABLO preparation. Air blowing is one of the well-known processes for changing the oil structure by forming hydroperoxide groups on the fatty acid chains. The importance of the hydroperoxide groups in the process is that they generated free radicals by thermal decomposition [1, 13, 16]. Free radicals are also formed by AIBN decomposition and hydrogen abstraction from the fatty acid chain by the generated free radicals. To get rid of confusion, the last two kinds of radicals were not included in Figure 4.1. It should be noted that the free radicals formed on the oil molecules favored the addition of styrene monomers to the oil moeity.

The polymerization mechanism in the presence of RAFT agent is explained in more detail in Figure 4.2.

As seen in Figure 4.2, blown oil initiator decomposes to form oil-derived and OH● radicals. The free radicals react with styrene monomer and form growing polymer chains (Pm● and HOP●). These growing radicals react with PMDC, and provide a thiocarbamate-ended chain and a new radical resulted from PMDC decomposition. No doubt that this radical initiates a new chain formation (Pn●). As seen the growing chains (Pm●, Pn●) undergo to equilibrium and termination reactions. The equilibrium reaction provides equal growing chance to the growing chains and lowered PDI.

In this work, the styrenation process with RAFT mechanism was conducted under miniemulsion condition in order to provide more homogenous reaction medium. ABLO with the hydroperoxide value of 448 meqperoxide-oxygene/kg.oil was prepared and used in the polymerization because in our previous study, styrenated oil could be successfully obtained with classical RAFT technique in solution by using the ABLO with the same level of hydroperoxide content [16]. AIBN was also added to the polymerization medium.



(*) **Reactions explained for $P_m^{\cdot}$ occur also with this growing chain.**

Figure 4.2 : Mechanism of the RAFT process for linseed oil-styrene copolymerization.

Miniemulsion polymerization allows one to obtain nano-sized polymer particles due to the almost constant droplet size throughout the reaction as a result of the advantages of miniemulsion systems compared to classical emulsion. It is well known that in classical emulsion polymerization monomer diffusion is essential for the progress of polymerization [49, 50]. In this context, free radicals are formed in water phase by decomposition of water soluble initiator and these radicals diffuse to the micelles and cause the monomers to polymerize leading to the generation of polymer particles. The size of polymer particles increases as the polymerization progress. Due to the increase in size and surface area, additional surfactant is necessary for the stabilization of the growing particles. This additional surfactant is supplied from the water phase and consequently, surfactant concentration falls below the CMC. Under this condition, micelles destabilize and their surfactants are used by growing particles as well. As polymerization progress, the monomer content of particles decreases and their monomer needs are supplied from monomer droplets. Consequently, monomers diffuse from the monomer droplets to the water phase and then the water-dissolved monomers diffuse to the polymer particles. In this way, the size of the monomer droplets become smaller througout the polymerization and finally they disappeared [49, 50].

In contrast to the above mentioned complex nucleation mechanism, ideal miniemulsion process takes place by droplet nucleation as a dominant nucleation mechanism [50, 59]. It should be emphasized that in this process, surfactant concentration must be lower than CMC. Under this condition, micelle formation is prevented and almost all surfactant is used to cover droplets. Therefore, nucleation and polymerization take place in the monomer droplets. If the monomer is slightly water soluble, homogeneous nucleation is also likely to occur to a small extent but generally it is ignored [50, 59].

In this study, since all ingredients including AIBN and ABLO are all water insoluble, aqueous phase nucleation is avoided in the polymerization. Thus, the hydrophobic structure of the ingredients forces the copolymerization to occur within the droplets. As explained before, in literature in order to decide whether the polymerization was miniemulsion polymerization or not, generally, the particle size only at the beginning and at the end of polymerization was taken into consideration. However, small differences in droplet/particle sizes even they are within the miniemulsion range, can

cause to a significant change in reaction progress. In the present study, by applying the above mentioned strategy, the best condition for miniemulsion polymerization was determined to provide that the size of droplet/particle should remain practically unchanged throughout the polymerization. In this way, the conditions of being 1:1 copy [59] for the droplets throughout the polymerization were satisified. In this context, first, surfactant concentration was determined to make ensure the elimination of monomer diffusion among droplets and coalescence of droplet/particles. For this purpose, the droplet/particle diameter was measured throughout the polymerization carried out at different amounts of CTAB as shown in Table 4.1. Droplet/particle size of all these samples was measured by DLS analysis. The measured effective diameters are given together with diameter polydispersities (D-PDI) and standart deviations for the SBO samples prepared under the conditions explained in Table 4.1.

Table 4.1 : Droplet/particle diameters and diameter polydispersities (D-PDI) for all SBO samples.

Sample	Reaction Time (h)	Effective Diameter (nm)	D-PDI	Standard Deviation of Effective Diameter
	0	179.6	0.091	
SBO-1	6	171.6	0.115	
	12	169.8	0.104	5.643
(CTAB: 8 %, by	24	173.6	0.108	
wt, of monomer)	48	164.1	0.127	
	0	167.0	0.111	
SBO-2	6	164.6	0.107	
	12	157.7	0.119	4.255
(CTAB: 16 %, by	24	168.9	0.124	
wt, of monomer)	48	165.4	0.141	
	0	155.5	0.116	
SBO-3	6	154.6	0.143	
	12	157.7	0.103	3.615
(CTAB: 32 %, by	24	154.0	0.098	
wt, of monomer)	48	148.0	0.134	
	0	150.7	0.097	
SBO-4	6	109.7	0.155	
	12	121.4	0.131	24.130
(CTAB: 64 %, by	24	112.3	0.141	
wt, of monomer)	48	83.7	0.262	

As seen, the smallest standart deviation was obtained in the case of SBO-3. By evaluation of the SBO-3 results, it is clear that the effective diameter remained practically unchanged during the course of reaction. This showed that coalescence of droplets and monomer diffusion to the polymer particles could be prevented under the applied condition. Due to this fact, additional experiments were not included in the study for further determination of optimal amount of HD the role of which is to create an osmotic pressure opposes diffusion of monomer from droplets. It is well known that this kind of mechanism is essential for miniemulsion polymerization and it makes the main difference between classical emulsion and miniemulsion polymerizations [50, 59, 133, 134].

The DLS graphs of SBO samples are also given in Figures 4.3-4.6. The level of uniformity of the effective diameters through the polymerization can be well followed visually from these graphs.

As seen in the miniemulsion polymerization the lowest polydispersity range (1.46-1.76) was attained in SBO-3 conditions. In order to understand the effect of miniemulsion conditions on the polydispersity index, the samples of the classical RAFT polymerization in dioxane were also prepared for the purpose of comparison and, as shown in Table 4.2, these samples have polydispersity index of 1.95 and 1.83 for 24 h and 48 h reactions, respectively. The RAFT miniemulsion gives styrenated oil samples with low polydispersity index being 1.71 and 1.76 for 24 h and 48 h, respectively. These PDI values are lower than those explained above for classical solution RAFT polymerization are. In addition, by examining the SBO-4 conditions, molecular weight distribution is higher (PDI values > 2) than SBO-3 conditions due to the loss of droplet stability. This instability is explained by the new nucleation locus with high surfactant content.

Furthermore, the conversion values of SBO samples were determined for each reaction time. Conversions and ln $[(M_0/M)]$ for all conditions are given in Table 4.3. The graphs of ln $[(M_0/M)]$ against time were constructed, as seen in Figure 4.12, and a straight line was obtained for each SBO sample. This indicated that the polymerization has controlled 'living' characteritics [136, 137].

Table 4.3: Conversion and $\ln[(M_0/M)]$ values for all SBO samples for each reaction time.

	SAMPLE							
Time	SBO-1		SBO-2		SBO-3		SBO-4	
	Conversion (%, weight)	$\ln[(M_0/M)]$	Conversion (%, weight)	$\ln[(M_0/M)]$	Conversion (%, weight)	$\ln[(M_0/M)]$	Conversion (%, weight)	$\ln[(M_0/M)]$
6	24.56	0.28183	24.50	0.28103	32.74	0.39660	30.0	0.35667
12	27.14	0.31663	25.52	0.29463	37.43	0.46888	41.40	0.53443
24	38.27	0.48240	33.43	0.40691	46.50	0.62548	47.0	0.63487
48	43.14	0.56457	44.10	0.58160	61.58	0.95659	64.0	1.02165

It is well known that the application of NMRP under macroemulsion conditions showed the colloidal instability [48, 138]. By taking this fact into account, in the current study this polymerization was carried out by macroinitiator method under miniemulsion conditions. In order to obtain a macroinitiator, linseed oil PGs were prepared and esterified with ACPC in order to insert thermaly libale azo groups into the oil-based initiator structure. ACPC was synthesized from ACPA by converting acid groups to acid chlorides by means of thionyl chloride [128]. Since the azo groups of ACPA is thermally liable, in the esterification reaction, acid chloride was used in order to perform the reaction at low temperature to protect azo groups from decomposition. Macroinitiator thus prepared was subjected to polymerization with styrene. The overall process and the representative structure of the styrenated oil sample is explained in Figure 4.13.

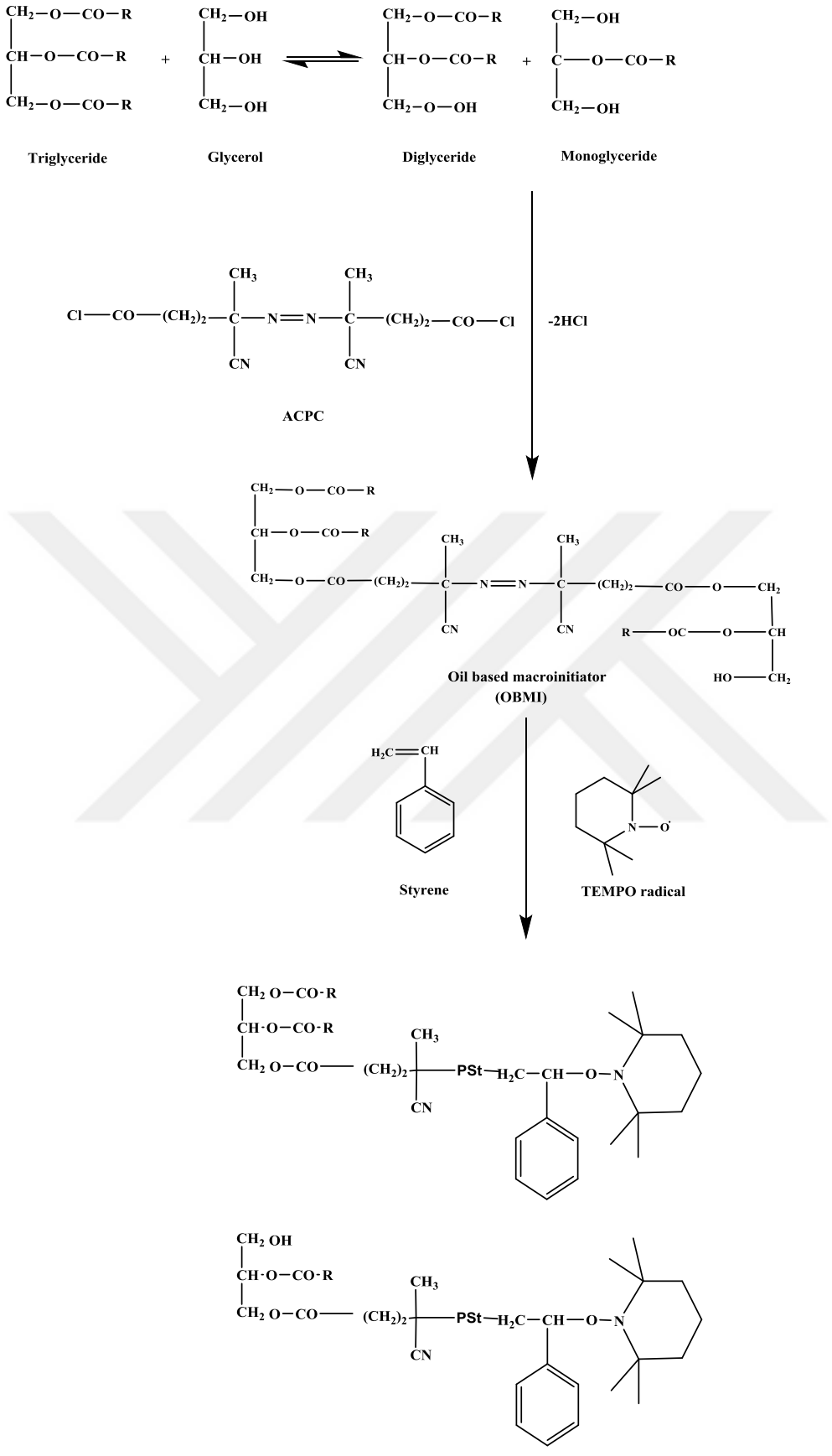


Figure 4.13 : Representative styrenated oil structure obtained by NMRP technique.

reaction. Additionally, in order to understand the effect of TEMPO amount, miniemulsion polymerization was carried out with OBMI/TEMPO ratio of 1/2 and the resulting sample (SO-TMP2(1/2)) showed lower molecular weight and PDI as 1.41. This PDI value is close to the results of NMRP carried out with ordinary monomers such as styrene and n-butyl acrylate [51, 52, 120]. It should be emphasized that although OBMI has a larger molecular weight, a low PDI value could be obtained due to its hydrophobic nature, which prevented the monomer diffusion. The another factor, as explained above, is the formation of radicals having molecular weight very close to each other.

Table 4.6 : The change of molecular weight and polydispersity of styrenated oil samples obtained in the presence of TEMPO in different reaction times in miniemulsion and solution polymerization conditions.

Sample	Time (h)	Mn[a]	Mw[a]	PDI[a]	Conversion[b] (%)
SO-TMP2	6	8465	13919	1.64	24.41
SO-TMP2	12	8829	16448	1.86	31.18
SO-TMP2	24	9330	16589	1.78	39.67
SO-TMP2 (1:2)	24	5720	8071	1.41	28.42
TMP-SOL[c]	12	9023	15520	1.72	29.13
TMP-SOL[c]	24	12561	25247	2.01	34.50

[a] Molecular weight estimated by GPC based on polystyrene standards.

[b] Conversion was determined gravimetrically.

[c] Samples prepared by NMRP in xylene.

Additionally, the conversion and ln [(M_0/M)] values are given in Table 4.7 for all SO-TMP1-3 samples. The graphs of ln [(M_0/M)] against time were constructed, as seen in Figure 4.24, and a straight line was obtained for each sample indicating that the polymerization has controlled 'living' characteritics for all samples [136, 137].

Table 4.7 : Conversion and ln [(M_0/M)] values for all SO-TMP samples for each reaction time.

	SAMPLE							
Time	**SO-TMP1**		**SO-TMP2**		**SO-TMP3**		**SO-TMP2 (1/2)**	
	Conversion (%, weight)	**ln[(M_0/M)]**	**Conversion (%, weight)**	**ln[(M_0/M)]**	**Conversion (%, weight)**	**ln[(M_0/M)]**	**Conversion (%, weight)**	**ln[(M_0/M)]**
6	21.14	0.2374	24.41	0.2798	17.56	0.1931	15.48	0.1682
12	27.44	0.3208	31.18	0.3737	26.47	0.3075	19.12	0.2122
24	32.18	0.3883	39.67	0.5053	34.14	0.4176	23.74	0.2710

5. CONCLUSION

In the first part of the thesis, RAFT polymerization was applied for ABLO-styrene system under miniemulsion conditions in order to obtain styrenated oil that is a well-known coating material. The miniemulsion polymerization was carried out under the experimentally determined ideal miniemulsion condition. In order to have comparative samples, the polymerization was also carried out in solution. PDI values were found to be 1.71 and 1.76 for the polymerization carried out under miniemulsion condition for 24 and 48 h, respectively. PDI values were also determined for RAFT polymerization in solution and found that 1.95 and 1.83 for 24 and 48h reaction times, respectively. PDI values in the miniemulsion polymerization were found to be smaller than those of solution polymerization although solution can be though as a more homogenous medium in comparison. It is well known that in the case of miniemulsion, complex nucleation mechanism of the classical emulsion was avoided and the reaction is occurred in the droplets in the absence of solvent. Due to this fact, PDI was found to be smaller in miniemulsion polymerization. Film tests showed that the prepared styrenated oil sample of miniemulsion polymerization could be used as an oil based binder.

In the second part of the thesis, it was aimed to obtain styrenated oil as a coating material by NMRP adapted miniemulsion polymerization. For performing miniemulsion polymerization , ideal surfactant concentration was experimentally determined. The polymerization was also carried out in xylene for comparison. Polydispersity indexes of SO-TMP2 sample were found to be 1.64, 1.86 and 1.78 for 6, 12 and 24h reactions respectively for the polymerization carried out in miniemulsion medium. As seen, PDI values in the miniemulsion polymerization was found closer to samples obtained in solution polymerization showed 1.72 and 2.01 PDI values for 12 and 24 h. Droplets are 1:1 copy of the initial droplets during the polymerization. In ideal miniemulsion condition experimentally determined, complex nucleation mechanism are avoided and the reaction is occurred in the droplets called as ‘nanoreactors’.

Finally, SO-TMP2 sample obtained in ideal condition was tested as an oil-based binder according to related standard test methods. Film test results showed that SO-TMP2 sample could be used as an oil-based binder with good flexibility, acid/water/alkali resistance and drying time.

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