ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

EMULSION POLYMERIZATION OF VINYL ACETATE BY URETHANE BASED SURFACTANT AND HIGH SOLID CONTENT WATER-BASED EMULSION POLYMERIZATION OF ACRYLIC MONOMERS

M.Sc. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

JUNE 2018

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

VİNİL ASETATIN ÜRETAN ESASLI SURFAKTAN İLE EMÜLSİYON POLİMERİZASYONU VE AKRİLİK MONOMERLERİN YÜKSEK KATI İÇERİKLİ SU BAZLI EMÜLSİYON POLİMERLERİNİN SENTEZLENMESİ

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To my lovely brother,

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ABBREVIATIONS

VAc : Vinyl Acetate
MMA : Methyl Methacrylate
BA : Butyl Acrylate
MAA : Methacrylic Acid
CMC : Critic Micelle Concentration
HLB : Hydrophilic Lipophilic Balance
HEC : Hydroxy Ethyl Cellulose
PVOH : Poly Vinyl Alcohol
GPC : Gel Permeation Chromatography
HSC : High Solid Content
MFFT : Minimum Film Formation Temperature
St : Styrene
nm : Nanometer
BPO : Benzoyl peroxide
AIBN : Azobisisobutyronitrile
HSC : High Solid Content
HSC/LV : High Solid Content / Low viscosity
PVAc : Poly**(**vinyl acetate)
P(MMA-co-BA): Poly**(**Methyl methacrylate-co-Butyl acrylate)
KPS : Potassium per sulfate
DI water : Deionized water
SLS : Sodium Dodecyl Sulfate
t-BHP : tert-Butyl hydroperoxide

SYMBOLS

η	**:** Apparent viscosity
ϕ	**:** The Volume Fraction
ϕ max	**:** Maximum Volume Fraction
M_n	**:** Number Average Molecular Weight
M_w	**:** Weight Average Molecular Weight
M_z	**:** Higher Average Molecular Weight
cP	**:** Centipoise
Tg	**:** Glass Transition Temperature

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EMULSION POLYMERIZATION OF VINYL ACETATE BY URETHANE BASED SURFACTANT AND HIGH SOLID CONTENT WATER-BASED EMULSION POLYMERIZATION OF ACRYLIC MONOMERS

SUMMARY

Emulsifiers, another name are surfactants, are characterized by a chemical structure comprising a hydrophilic group having one and/or two hydrophobic flexible alkyl chains of a certain length. In small quantities dispersed in the aqueous phase, the surfactant is adequate for self-assembly into the micelle micro aggregates.

Surfactants are used in several areas for different purpose such as painting, emulsion polymerizations, adhesives, textile industry, etc. Surfactants are divided into four main categories. They are anionic, cationic, non-ionic and zwitterionic.

In this study, a new nonionic polymeric surfactant (PU) has been synthesized with the reaction between Poly(ethylene glycol) dimethyl ether (PEG500) and Toluene 2,4-diisocyanate (TDI).

The polymeric surfactant was characterized by using FT-IR spectroscopy, GPC, critical micelle measurements via tensiometer.

Critical micelle concentration of PU was determined by surface tension measurements. This value was calculated as 0.68x10 mg / mL.

Molecular weight of the PU was determined by gel permeation chromotography (GPC). M_w, M_n and M_z molecular weight was measured as respectively 1361, 1163 and 1524 g / moles. Polydispersity index was obtained as 1.171 .

PU was used emulsion polymerization of vinyl acetate and copolymerization of metyl methacrylate and butyl acrylate depending on surfactant quantity and time. Obtained latexes was characterized by particle size measurements, viscosity and surface tension measurements. In addition, molecular weight of the polymers were determined by GPC.

High solid content water-based emulsion polymerization studies were performed in the another part of the thesis.

Latexes produced by emulsion polymerization are versatile materials. It extensively used in very different industry such as adhesives, coatings, textiles, paper paints, floor polish and makeup. The solids content of the latexes produced in the industry is between 50-55%. High solids content (HSC) brings many advantages, such as maximizing reactor production, minimizing transportation and storage costs, providing greater flexibility in product formulation and improving surface coverage when applied.

The increase in solids content negatively affects the latex viscosity. This also affects the heat removal rate, mixing ability, mass transfer and product stability. The way to obtain low viscosity (HSC / LV) high solids content is achieved by

controlling the particle size distribution (PSD). Particles in a perfect monodisperse latex will contact the solids content of about 64% theorically. This explains that most industrial processes with relatively narrow particle size distribution generally operate at less than 55% by weight of solids content. Bimodal particle size distribution production is considered to come from above this limitation and to achieve the goals of high solids content and low viscosity.

In this thesis, two different methods were used to produce twelve different high solid content emulsion polymerization.

Firstly 42 nm seed emulsion was prepared by semi-continuous polymerization. Seed emulsion was grown with pre-emulsion via feeding. After the firstly added seed is required to grow, a precise amount of seed was introduced into the reactor shot wise, keeping the feeding of monomers, surfactant and ammonia to reach the desired solids content.

Secondly, primary seed was not used in second method. The rest of experiment conditions are same with first method.

65% solid content latexes are obtained. The latexes were characterized by using, Brookfield viscometer, tansiometer, Zetasizer Nanaoseries NS.

Unimodal particle size distributions were obtained at the final product that is produced with first method. Viscosities of these products are quite high, compared with other method. The surface tension of these products raise with increasing solid content.

Another products which are produced second method, has bimodal particle size distribution. Viscosities of these products are quite low, due to bimodality. The surface tension of these products has nearly same values because of surfactant amount.

To sum up, high solid content low viscosity bimodal and unimodal particle size distribution emulsion polymers were synthesized.

VİNİL ASETATIN ÜRETAN ESASLI SURFAKTAN İLE EMÜLSİYON POLİMERİZASYONU VE AKRİLİK MONOMERLERİN YÜKSEK KATI İÇERİKLİ SU BAZLI EMÜLSİYON POLİMERLERİNİN SENTEZLENMESİ

ÖZET

Yüzey aktif maddeler, hidrofilik grup ve bir ya da iki tane hidrofobik, ortalama uzunlukta, alkil zincirine sahip maddeler olarak karakterize edilip, ayrıca emülgatör ya da surfaktan olarak da adlandırılırlar. Sulu fazda misel oluşturmak için çok az miktarda yüzey aktif madde yeterlidir.

Yüzey aktif maddeler endüstriyel açıdan çok önemlidirler. Boya sektöründe, emülsiyon polimerizasyonlarında, yapıştırıcı ve tekstil gibi birçok endüstride yüzey aktifler kullanılmaktadır. Anyonik, katyonik, non-iyonik ve amfoterik olmak üzere 4 çesit yüzey aktif mevcuttur.

Bu çalışmada, toluen 2,4-diizosiyanat (TDI) ve poli(etilen glikol) dimetil eterin (PEG500), dibütil tin laurat katalizörü varlığında reaksiyonu ile yeni bir noniyonik yüzey aktif madde sentezlenmiştir.

Bu polimerik yüzey aktif maddenin karakterizasyonu çeşitli cihazlar ve yöntemler kullanılarak yapılmıştır.

Kritik misel konsantrasyonu tayini için yüzey gerilim cihazı kullanılmıştır. Bu değer 0.68x10 mg / mL olarak hesaplanmıştır.

Polimerik yüzey aktif maddenin moleküler ağırlığı GPC ile tayin edilmiştir. Sayıca ortalama, ağırlıkça ortalama ve z-ortalama molekül ağırlıklıkları sırası ile 1361, 1163 ve 1524 gr / mol'dür.

Tayin edilen polimerik sürfaktan farklı miktarlarda kullanılarak Vinil asetatın emülsiyon polimerizasyonu yapılmıştır. Emülgatör miktarına ek olarak reaksiyon sürelerinin de etkisi incelenmiştir.

Karşılaştırma yapmak amacıyla ticari emülgatör Dowfax 2A1 ile aynı reaksiyonlar tekrarlanmıştır. Dowfax 2A1 ile yapılan emülsiyonların viskoziteleri daha düşük ve görünümleri açık mavi-beyaz renktedir.

Poliüretanbazlı emülgatör ile yapılan çalışmaların viskozitesi biraz daha yüksek ve görünümü sütsü-beyaz renktedir.

Dowfax 2A1 ile yapılan çalışmaların sayıca ortalama molekül ağırlıkları ve kütlece ortalama molekül ağırlıkları, sentezlenen poliüretan bazlı yüzey aktif madde ile yapılan emülsiyonların molekül ağırlıklarından oldukça yüksektir.

Dowfax 2A1 ile yapılan emülsiyonların, emülgatör miktarı arttıkça yüzey gerilimi azalmıştır.

Sentezlenen yüzey aktif madde ile yüksek katılı emülsiyonlar sentezlemek için bütil akrilat ve metil metakrilat monomerleri ile ön denemeler yapılmıştır. Emülgatör miktarı iki katına çıkarıldığında yeniden çekirdeklenme gözlemlenmiş ve iki farklı

parçacık boyutu gözlemlenmiştir. Sayıca ve ağırlıkça ortalama molekül ağırlıkları veyüzey gerilimleri emülgatör oranı artırıldığında kayda değer bir biçimde azalmıştır.

Lateksler yapıştırıcı, kaplama, tekstil, kağıt boyaları, zemin cilası ve makyaj sanayi gibi alanlarda yaygın olarak kullanılan çok yönlü malzemelerdir.

Reaktör üretimini en üst düzeye çıkarmak, nakliye ve depolama maliyetlerini en aza indirmek, ürüne daha fazla esneklik kazandırmak, enerjiden ve iş yükünden tasarruf etmek ve uygulanırken yüzey kapsamının geliştirilmek ve iyileştirmek için yüksek katı oranlı lateksler birçok endüstride çalışılmaktadır.

Lateksin viskozitesi, katı madde içeriğiyle birlikte keskin bir şekilde artar; bu da katılaşma derecesini, karıştırma, kütle transferi ve kararlılığı etkiler. Düşük viskoziteler ile yüksek katı içeriği elde etmenin anahtarı partikül boyutu dağılımının (PSD) kontrolüdür.

Mükemmel tek dağılımlı bir lateksdeki parçacıklar yaklaşık kütlece % 64 katı içeriğinde birleşmeye başlarlar. Bu, parçacık boyut dağılımı nispeten dar olan çoğu endüstriyel prosesin genelde katı madde içeriğinin ağırlıkça % 55'inden azında çalıştığını açıklar. Bu kısıtlılığın üstesinden gelmek ve yüksek katı içeriği ve düşük viskozite hedeflerini başarmak için bimodal partikül dağılımlı emülsiyonların üretimi düşünülmüştür.

İki farklı yöntem kullanılarak on iki adet yüksek katılı emülsiyon polimerleri elde edilmiştir. Öncelikle 42 nm boyutlu tohum emülsiyonu hazırlanmıştır.

İlk yöntemde belirli bir miktarda tohum emülsiyonu reaktöre alınıp preemülsiyon (monomer, emülgatör, amonyak ve su) ve başlatıcı ile dengeli bir şekilde üç saat boyunca beslenmiştir. Beslemenin ikinci saatinde ortama başta eklenen tohumun 5,10 ve 15 katı oranında ortama hızlı bir biçimde 42 nm boyutlu tohum tekrardan eklenmiştir ve dengeli beslemeye devam edilmiştir. Bu şekilde %60 ve %65 katılı emülsiyonlardan altı tanesi hazırlanmıştır.

İkinci yöntemde ortama tohum eklenmeden polimerizasyona başlanmış ve dengeli ilavenin ikinci saatinde ortama üç farklı oranda 42 nm boyutlu tohum eklenmiştir ve dengeli beslemeye devam edilmiştir. Bu şekilde de %60 ve %65 katılı emülsiyonlardan geriye kalan altı tanesi hazırlanmıştır.

İlk yöntemle yapılan ürünlerde (ön tohum ilaveli) monomodal partikül dağılımı, ikinci yöntemle yapılan ürünlerde (ön tohum ilavesi olmayan) bimodal partikül dağılımı elde edilmiştir.

%60 katı maddeli, ön tohumlu emülsiyon polimerlerinin partikül boyutları yaklaşık 200 nm civarlarında ve monomodaldir. Partikül dağılımı ile viskozite değerleri birbirlerine uyumlu sonuçlar vermiştir. %65 katı maddeli, ön tohumlu emülsiyon polimerlerinin partikül boyutları yaklaşık 220 nm civarlarında ve monomodaldir. %65 katı maddeli latekslerin viskoziteleri oldukça yüksek çıkmıştır. Bunun sebebi 100 ila 200 nm arasında bir lateks partikül büyüklüğünün, ağırlıkça 50 katı ila ağırlıkça% 55'e kadar akışkanlıklarını koruduğu şeklinde literatürlerde açıklanmaktadır. Latekslerin yüzey gerilimleri katı madde miktarı arttıkça artış göstermiştir.

Ön tohum ilavesi olmayan latekslerin viskoziteleri oldukça düşük çıkmıştır. Bu durum partikül boyut dağılımının bimodal olmasından ve partikül büyüklüğünün fazla olmasından kaynaklanmaktadır.

Latekslerin yüzey gerilimleri yaklaşık olarak tüm örneklerde eşittir. Bu da surfaktan oranlarının benzer olmasından kaynaklanmaktadır .

Sonuç olarak; bimodal ve monomodal parçacık boyut dağılımına sahip, düşük viskositeli lateksler elde edilmiştir. Bu sayede; reaktör üretimini üst düzeye çıkarılmış, enerjiden ve iş yükünden tasarruf edilmiştir.

Büyük boyutta üretimlere geçildiğinde; reaktör üretimini üst düzeye çıkarmak, nakliye ve depolama maliyetlerini en aza indirmek, ürüne daha fazla esneklik kazandırmak, enerjiden ve iş yükünden tasarruf etmek mümkün olacaktır.

Sonuç olarak; bu tezde iki farklı konu çalışılmıştır. İlk olarak, yeni noniyonik poliüretan esaslı yüzey aktif madde (PU), metoksi PEG-500 ve TDI'dan başlayarak sentezlendi.

PU, vinil asetat (VAc) ve Metil metakrilat (MMA) -Butil akrilat (BA) kopolimerizasyonunun emülsiyon polimerizasyonunda kullanıldı. Elde edilen lateksler 3 ay boyunca stabil kaldı.

Emülsiyon polimerizasyon deneyleri, süreye ve sürfaktan miktarına bağlı olarak çalışıldı. Aynı zamanda, bu deneyler anyonik yüzey aktif madde (Dowfax 2A1) kullanılarak tekrarlandı. Farklı sürfaktanları kullanarak elde edilen lateksler, viskozite, yüzey gerilimi, parçacık boyutu ve moleküler ağırlık ölçümleriyle karakterize edildi.

Tezin ikinci bölümünde, akrilik monomerlerin yüksek katı içerikli su bazlı emülsiyon polimerizasyonları yapıldı.

Reaksiyonların sonunda %60-65 katı içerikli lateks elde edildi ve partikül büyüklükleri belirlendi ve bimodal sistem başarıyla elde edildi.

Latekslerin partikül büyüklüklerinin belirlenmesinin yanı sıra, viskozite, yüzey gerilimi ve moleküler ağırlık ölçümleri gibi diğer özellikler araştırıldı.

Ayrıca sentezlenmiş olan poliüretan bazlı yüzey aktif madde ile anyonik yüzey aktif madde, yüksek katılı emülsiyon polimerleri daha sonraki çalışmalarda denenecek ve sinerjik etkilerinin olup olmadığı araştırılacaktır.

1. INTRODUCTION

Emulsion polymerization derived from acrylic monomers is a diverse and versatile family of the most composition of the broadly commercially important broad emulsion polymer classes. 30% of commercial emulsion polymers account for acrylic based polymers. Acrylic and methacrylic monomers have the ability to copolymerize each other finely. These provide to widely range of composition and physical properties like a solubility characteristic and glass transition temperature.

In 1930, the acrylic emulsion, poly (ethyl acrylate), is produced for textile and leather application. Since 1953, commercial important of acrylate based emulsions increase. MMA/EA copolymer is the first emulsion copolymer for paints, it provide oxidative stability and light stability when applied on surface. Acrylic latexes have the widest range of applications in paints and coatings. Besides, acrylic latexes commonly used in paper, sealant, waxes, graphic arts, cement additives, adhesives, non-woven fabrics and polishes.

The glass transition temperature of high-volume commercial polymers produced from acrylic monomers can raise from -80 to 100 ^{o}C. In addition, the solubility characteristics of these polymers are completely soluble in oil and can be polar. All of these properties provide wide application market from the highly soft pressure sensitive adhesives to film forming of paints, to hard composition for polishes and pigments. A valuable feature of the emulsion polymer chemistry of acrylic is ability to incorporate a wide range of functional chemical groups that can provide sites for crosslinking, compatibility with other polymers, polymerization reactions, adhesion, and biochemical activity.

Acrylate monomers which include a vinyl group and a acid group on structure used to produce acrylate polymers. Acrylate monomers are derivatives of acrylic acid for instance, methyl methacrylate in which one vinyl hydrogen and the carboxylic acid hydrogen are both replaced by methyl group. By building block monomers is meant a subset of high commercial volume low cost monomers used to adjust the bulk

physical properties of the bulk of the polymer backbone composition such as chemical and radiation susceptibility, glass transition temperature and solubility.

Water-borne acrylic dispersions are widely prepared via emulsion polymerization. It has more advantages when compared to solution polymerization. In emulsion polymerization, high molecular weight polymer synthesis on the industrial scale and high solids polymers can be produced and other advantage is that the resin which has low viscosity, thus allowing fast air-drying via evaporation of water.

High solid content (HSC) latexes are described as having more than 60% solid content. Compared to traditionally latexes which have 40-50% solid, high solid content latexes have distinguished properties due to advantages such as maxizing the production, minimizing the energy consumption, transportation cost and storage capacity, providing flexible last product formulation, decreasing the film-forming time and developing surface coverage.

2. THEORICAL PART

2.1 Emulsion Polymerization

Emulsion polymerization has been described as a technological, scientific and commercially significant reaction developed during World War II. It is by virtue of the require to substitute the latex of natural rubber [1].

Emulsion polymerization has beneficial properties, which are producing high molecular weight polymers, being negligible volatile organic compound. Moreover, its reaction medium is generally water and ensures a naturally safe process. Therefore, the annual production of emulsion polymerization is more than 20 million tones at the present time. The reason for this is that emulsion polymerization is widely used in various sectors comprising papers, textiles, adhesives, paints, construction materials, binders for nonwoven fabrics, cosmetics and drug delivery systems [2].

2.2 Mechanism of Emulsion Polymerization

In emulsion polymerization, which is a kind of free-radical polymerization, monomer mixtures are dispersed in aqueous phase with the help of proper emulsifiers. The polymerization reaction happens at raised temperatures. It is initiated by water-soluble initiators and take place in micelles.

Several mechanisms have been suggested for latex particle formation and the most crucial qualitative mechanism of emulsion polymerization was recommended by Harkins in 1945 and 1946 [3,4]. On the other hand, another important mechanism of emulsion polymerization was proposed by Smith and Ewart. They conduct to attain first quantitative theory for emulsion polymerization. Moreover, it comprises of equations for designating the rate of polymerization and the sum of latex particles.
These theories have been carried out just in conditions;

a) in presence of “hydrophobic monomers”
b) in the presence of water-soluble initiators

c) nonspecific, micelle-forming emulsifiers

d) above the critical micelle concentration(CMC).

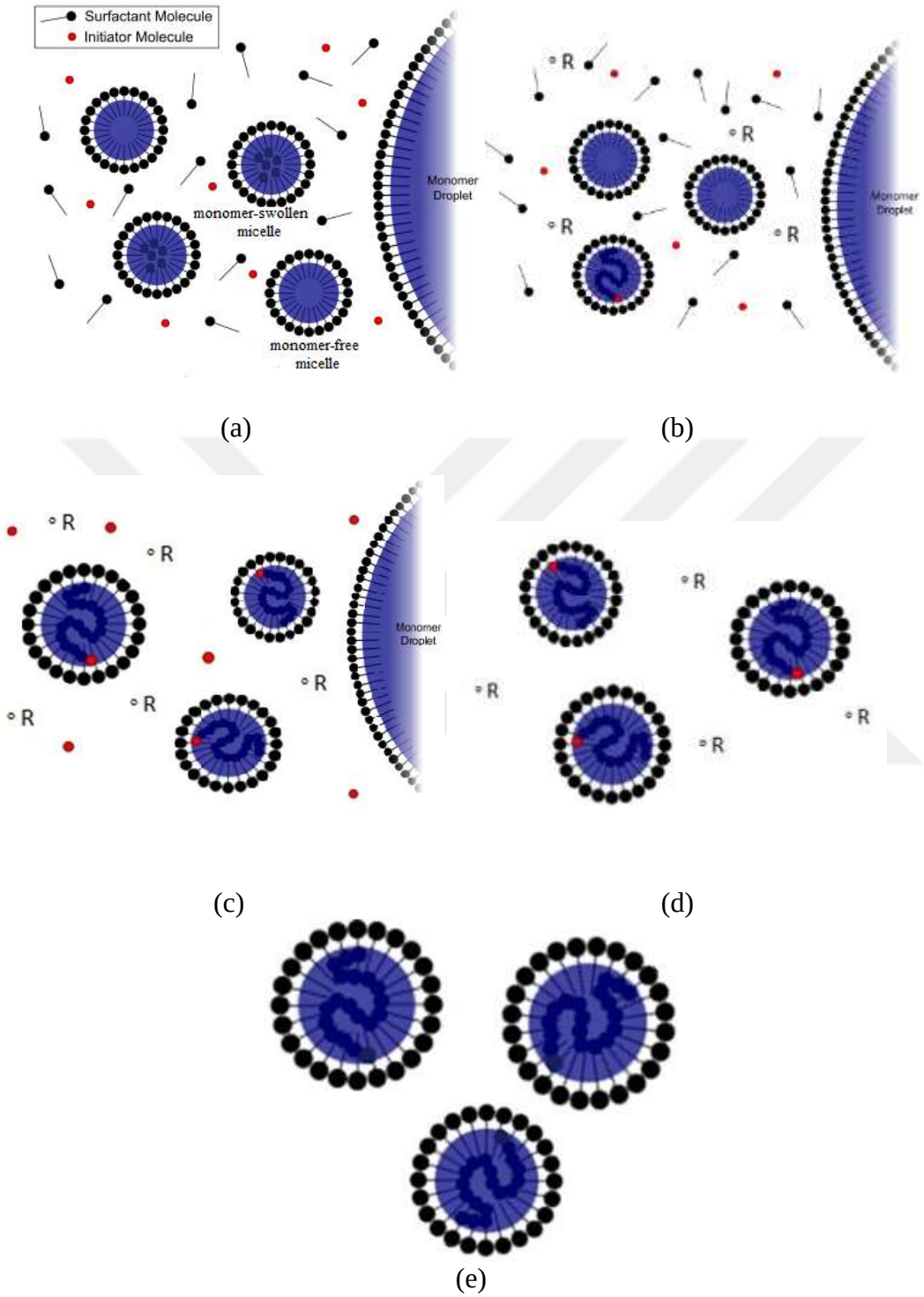


Figure 2.1 : Schematic representations for the mechanism of emulsion polymerization[5,6]

Harkins theory is illustrated in Figure 2.1 [5,6]. This theory can be explained by the fact that monomer droplets (1-10 microns in diameter) are dispersed in the water

phase at the beginning of the polymerization with the aid of an emulsifier and, monomer-swollen micelles (5-10 nm in diameter) can be in existence this system. The emulsifier concentration is above the critical micelle concentration at this condition. Nearly 1% of the total monomer is dissolved by the micelles. A negligible amount of monomer is soluble via water. The rest of total monomers are used in polymerization throughout the reaction. As a shown on Figure 2.2.a monomer-free micelles and a few amount of molecular soluble surfactant can occur. Polymerization is started by adding of initiator in a system after the micelles established and monomer phase dispersed in micelles. Emulsion polymerization mechanism comprise of three interval according to the Harkins, Smith and Ewart's theory. These mechanisms include initial stage, secondly the particle growth state and lastly completion state.

The initial stage (Interval I): Another name of this stages are "particle formation" or "particle nucleation". By adding the initiator to the reaction mixture, polymerization is started by free radicals. These are produced in the water phase with several ways. The primary site for the initiation of the polymer particle core is the micelle in that it exhibits a massive oil-water interface area for the diffusion of free radicals. Free radicals spread into monomer-swollen micelles that possess high monomer concentration. Conversely, in, a small amount of particle initiation may happen. The monomer molecules dissolved in continuous water phase and polymerization start by free radicals. This used to conclude the raised hydrophobicity of oligomeric radicals. The resulting polymers become very hydrophobic when they exceed their critical length. For this reason, the monomer shows a strong tendency to enter the swollen micelles. The follow that these monomer molecules enter the reaction and continue to grow. However, this nucleation occurs less important in compared to the others. The reason is that an increase in the amount of emulsifier in the system. By the reason of their small surface area for spreading of the free radicals, the amount of polymerization happening where the monomer droplets is considered as being a minor proportion of the entire amount. As a result, the monomer-swollen micelle is suitable as nucleation zones of polymer particles. This nucleation mechanism proposed by Harkins, Smith and Ewart. It is referred to as "micellar" or "heterogeneous" nucleation, which is altered by Gardon.Follow the nucleation occurred; the monomers continue to polymerize in their monomer-swollen micelles and are converted into polymer particles swollen with monomer.

Subsequently, monomers are permanently obtained from the monomer droplets by diffusion through the water phase. It use in the reaction location by polymerization process. Therefore, the micelles build up from tiny groups of emulsifier and monomer molecules to larger groups of polymer molecules got under control emulsion by the action of the emulsifier molecules located where the outer surfaces of the particles [5,6]. Emulsifiers, which supplied from the aqueous phase, ensure the colloidal stability of the growing particulate core. Respectively, this tends to cause decomposition of the micelles, including the monomer, which the polymerization has not yet begun. The micelles, which sustained adsorption of micellar emulsifiers above growing particles, begin to disappear (Figure 1.b). Interval I concludes with this disappearance of the micelles at comparatively early in which the reaction (e.g. between 10% and 20% conversion).

During Interval I, As the rate of polymerization increases, the reaction time increases and only one of every 100-1000 times, a polymer particle occurs. In accordance with the Smith-Ewart theory, the number of particles, which is nucleated per unit volume of water (Np), is proportional to the emulsifier concentration and initiator concentration to the 0.6 and 0.4 powers, in turn [3,4]. This number remains comparing with constant toward the end of polymerization follow that the particle nucleation process is accomplished.

The particle growth stage (Interval II): In this part polymerization, continue properly in the polymer particle until the monomer concentration is remained stable by monomer diffusion from the monomer droplets to micelle. In this stage, rate of polymerization is stable and monomer-swollen polymer particles and the ratio of monomer/polymer steady. The more size of the polymeric particle raise, the less size of monomer droplets. When the polymer conversion rise at 50.00-80.00 %, droplets of monomer start to evanish and the interval II ends. This situation was shown on the Figure 2.2.c. The unreacted monomers stay in polymer particles withal, all of the surfactant molecules stay on the surface of polymer particles.

The completion stage (Interval III): Interval III is the final stage of reaction. Throughout the interval I and interval II, polymerization continues. Ideally, throughout this stage, number of reaction locus is fundamentally fixed at number that it had happen established at the end of Interval I. On the other hand, the monomer concentration in the system continues to decrease towards the end of

the polymerization. Also rate of polymerization decrease. When all of the monomers convert to polymers (100%), polymerization is complete and polymer particles fixed with the surfactant. Final stage of polymerization is shown on Figure 2.2.e.

2.3 Ingredient of Emulsion Polymerization

The fundamental ingredients in an emulsion polymerization are the aqueous phase (water), a monomer, which is no soluble or quite a little soluble with water, an surfactant, and a initiators which take free radicals in the aqueous phase [8]. Different auxiliaries such as buffers, antimicrobial agents, acids, UV-absorbers, anti-aging agents, biocides, chain transfer agents , coalescing aids, plasticizers, thickening agents, bases, antioxidants, pigment and fillers etc. can be used emulsion polymerization recipes for gain various properties. The complexity of an auxiliaries, and the susceptibility of the system kinetics, mean that small changes in recipe or reaction conditions lead to unacceptable changes in the quality of the product [8].
The water is a chief ingredient in emulsion polymerization. As the continious phase;
It act to maintain a low viscosity, provide good heat transfer, serve to isolate the polymerization loci. Natural water contain mineral (inorganic), organic, gas phase component (calcium, magnesium, sodium, sulfate, nitrate, phosphate, oxygen…). Therefore, it can be lead variation in particle nucleation and stability, variation in particle size and destabilization problem. These problems are suppressed by using of deionized water in emulsion polymerization.

2.3.1 Monomer

Free-radical polymerizable monomers are necessary for emulsion polymerization. According to global production, vinyl chloride, butadiene, acrylate ester and methacrylate ester monomers, vinyl acetate, styrene, acrylic acid and methacrylic acid and, acrylonitrile are used in emulsion polymerization widely. The monomers, which have different chemical and physical properties, can be remarkable effect on end-product. According to the nature of monomers in aqueous phase emulsion polymerization can be classified into three groups.

a) Good soluble in water (acrylonitrile)
b) Limited solubility in water (1-3%) (methyl methacrylate and other acrylates)
c) Insoluble in water (styrene, butadiene, vinyl chloride, isoprene, etc.)

d) Different initial polymerization rates and different solubility are due to monomeric solubility in water.

Monomer selection involves several considerations. They are selected to satisfy a purpose and will dictate the basic physical, chemical, and thermal properties of the latex. The glass transition temperature (Tg) of latex particles greatly influences monomer selection. The Tg of a polymer is the temperature at which the polymer transitions from a hard, brittle, glass-like state to a soft, flexible, rubbery state. To yield continuous films, target particle polymer Tg must be well below ambient temperature. This allows sufficient polymer mobility for the interdiffusion of particle chains during film formation. In addition, the degree of stiffness and strength of a film varies with the concentration of monomer used.

Desired properties are rarely achieved with the use of one monomer, and instead, a balance of multiple monomers is often considered to yield a copolymer with the desired properties. Rubbery polymers will contribute to flexibility, adhesion, and tackiness while glassy polymers contribute to hardness, strength, and clarity. The glass transition temperature (*Tg*) of a copolymer is estimated by the Fox equation to establish the weight fractions (*W*) of each monomer required. Fox equation is indicated below (1):

$$\frac{1}{T_g} = \frac{W_{m1}}{T_{g\,m1}} + \frac{W_{m2}}{T_{g\,m2}} + \frac{W_{m3}}{T_{g\,m3}} \dots \quad (1)$$

2.3.2 Initiators

Emulsion polymerization is a complex process in which radical addition polymerization continues in a heterogeneous system.

The initiator produces free radicals, polymerization starts, which in turn cause to the propagation of the polymer. Thermal decomposition and redox reaction are two main reason to producing free radicals. Peroxidisulfates are most widely used as water-soluble initiators. For instance; potassium persulfate, sodium persulfate, and ammonium persulfate, which are decomposed by thermal energy between 70-90 ^{o}C. Decomposed two sulfate radicals anion, initiate the reaction. Peroxides and also thermal activation initiators are dissolved in water phase and monomer-swollen polymer phase. In contrast to water-soluble peroxide initiators, benzoyl peroxide

(BPO) and azobisisobutyronitrile (AIBN) are oil-soluble initiators which are used as thermal initiator in emulsion polymerization.

Another initiation system is redox reaction, which release free radical by the way of oxidation-reduction reactions. One of the advantages of redox initiation system is that reaction can be performed at low temperatures. Also chain branching and crosslinking in the synthesis of rubber are decrease at low temperature. In general, the redox couple reacts to produce radicals. During the emulsion polymerization process, one or both components must be fed. Redox initiator systems, which are, provide to control of temperature changes, a good helpful way for safety in emulsion polymerizations. The best-known redox initiators redox system is peroxodisulfate–bisulfite:

$$S_2O_8^{-2}– + HSO_3– \rightarrow SO_4^{-2}– + OSO_3^{-} + OSO_2H$$

Another initiator type is surface active initiators (inisurfs) for example, 2,2'-azobis (N-2'-methylpropanoyl-2-amino-alkyl-1-sulfonate)s and bis[2-(4'-sulfophenyl)alkyl]-2,2'-azodiisobutyrate ammonium salts . Inisurfs which keep stabilizing groups in their structure, without stabilizers emulsion polymerization which is more than %50 high solid content can be conducted by only inisurfs [1]. Free radicals can be created by also ultrasonically, or radiation-induced. Most generally used radiation-induced initiation system is 60Co γ-radiation in emulsion polymerization.

2.3.3 Surfactant

Emulsifiers, which are surface-active materials, also called as surfactant, dispersing agent, soap and detergents to decrease the surface tension of a liquid, provide easier spreading and can diminish the interfacial tension between two liquids phases.

Surfactant, which includes long-chain hydrophobic group and hydrophilic head group, can be classified in compliance with nature of this head group. Surfactants are very significant compound for emulsion polymerization and they play a key role for decreasing the interfacial tension between the water phase and monomer phase.

If these materials are used over the critical micelle concentration (CMC), they will create micelles, which are ordinated clusters of surfactant molecules. Moreover, monomer phase which dispersed in water phase by virtue of surfactant, become to form emulsion. During the polymerization they provide to stabilizing the growing latex particles [9].

2.3.4 Other ingredients

The recipes of commercial emulsion polymerization, which are usually much more complicated, may include a several type of ingredients.

Chain Transfer Agents:

To decrease the molar mass and regulate the molar mass distribution chain transfer agent are usually added to emulsion polymerization recipes. The most known chain transfer agents are mercaptans. The mercaptan and monomer phase feeded into the reactor during de emulsion polymerization. Consumption of monomer inside should be balanced with mercaptan consumption.

Buffer:

Buffer is preferred to regulate the pH of the polymerization locus. Sodium bi carbonate is frequently used buffer in emulsion polymerization. They also prohibit hydrolysis of the emulsifier and maintain the initiator efficiency. Buffers are often salts and as such they can influence the colloidal stability of the latex and particle size distribution.

Sequestering Agents:

If redox system is carried out, metal ion can be found in emulsion polymerization recipes. These metal ions may precipitate in fundamental aqueous medium. Sequestering agents are used to prevent precipitating of metal ions in a medium.

Biocides:

Biocides are used to prevent infestating of the dispersions by microorganism like a bacteria, moulds and yeasts throughout storage and transport. Generally, they are formed active substance combination of methyl- and chloromethyliazolinones, or else formaldehyde or formaldehyde donors [10].

Deformers:

Deformers are used low amount, in order to preserve the formation of extreme foam or micro foam along reaction, handling and transport.

UV light absorbers:

Latex polymers are also susceptible to UV radiation. UV light absorbers are therefore often included to absorb damaging low-wavelength radiation.

2.4 Surfactans

Surfactants, which are wetting agents that decrease the surface tension of a liquid, provide easier spreading. The word ‘Amphipathic’ comes from two Greek roots. Firstly, the affix amphi which means "double", "from both sides", "around” and then the root philos which expresses friendship or affinity. Surfactants are amphipathic molecules that contain least one solvent-loving group and one solvent-fearing group in their structure [11]. When the emulsifier is to be used in aqueous solution or water, then the previous terms hydrophilic and hydrophobic are used. Moreover, surfactants, consist of at least one polar one non-polar group in their structure, are dissolve in both organic solvents and water. Simplified surfactant structure is showed at Fig 2.3.

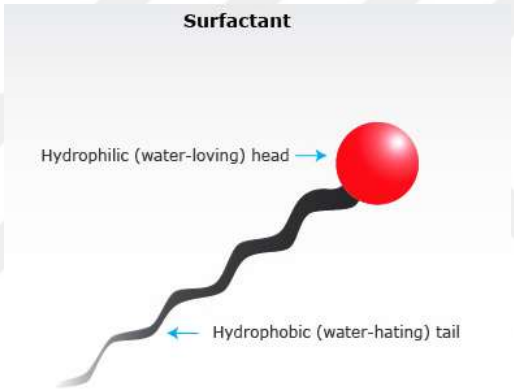


Figure 2.2 : Simplified surfactant structure

Surfactants carry out a lot of significant functions in emulsion polymerizations like as;

a) Decrease the interfacial tension among the aqueous phase and monomer, and stabilize the monomer as a emulsion

b) If surfactants are added in reaction loci over the critical micelle concentration, micelles will be happen. They are regular clusters of emulsifier molecules

c) The emulsifier helps to dissolve the monomer in the micelles

d) Stabilizing the growing latex particles and final latex particles

e) Acting to solubilize the polymer, chain transfer agent and/or retarders

f) Help to polymer nucleation by forming micelle [11-17].

Surfactants can be categorized into nature of head groups, which are anionic, cationic, Zwitterionic or non-ionic (Figure 2.4).

a) Anionic surfactants, which have negatively charged hydrophilic part

b) Cationic surfactants, which have positively charged hydrophilic part

c) Amphoteric surfactants, which has anionic and cationic properties based on the pH of the medium

d) Non-ionic surfactants, where the hydrophilic part is not charge.

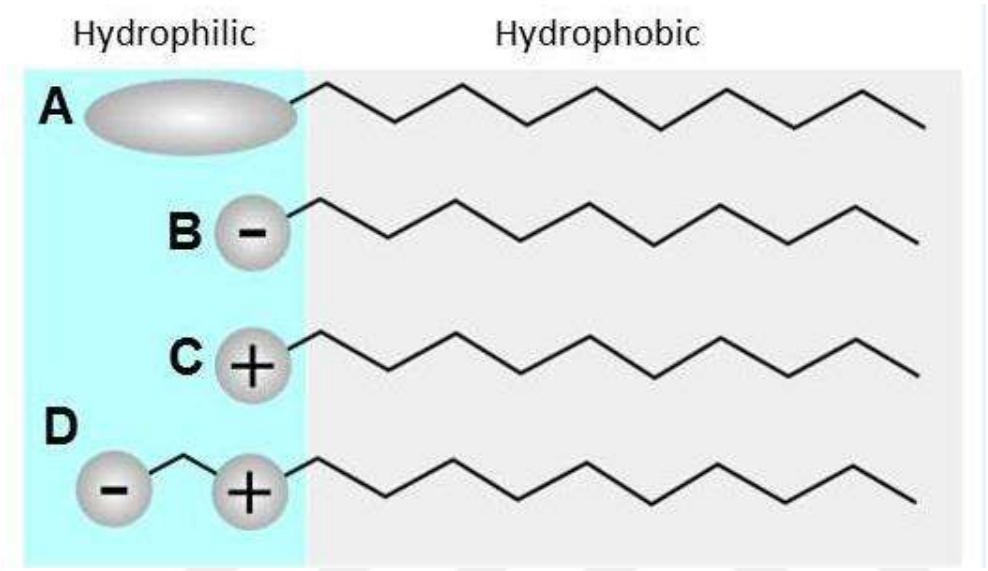


Figure 2.3 : Classification of surfactant

Most commonly used surfactants are nonionic and anionic because enhanced compliance with negatively charged polymer particles compared to other types of surfactants. Also, many emulsion polymerization recipes contain combination of surfactants to improve latex' colloidal stability. A HLB (hydrophilic- lipophilic balance of the polar and nonpolar components) value important for understanding proficiency of emulsification. Low HLB (beloved or 7) value is preferred for water-in-oil emulsions and higher HLB value is good for oil-in-water emulsions.

2.4.1 Anionic surfactants

The negatively charged hydrophilic head group of anionic emulsifier can contain sulfate, sulfonate or phosphate group attached on higher fatty hydrophobic backbone. Hydrophilic group can effect hydrolysis degree, pH, and latex stability and electrostatic stabilization.

Hydrophobic group may influence CMC value, the interfacial tension and adsorption behavior of the surfactant. Widely used anionic surfactants are sodium dodecyl benzene sulfonate, [$C_{12}H_{25}C_6H_4SO^{3-}Na^+$] sodium lauryl (dodecyl) sulfate,

[$C_{12}H_{25}OSO^{3-}Na^{+}$], and sodium dioctyl sulfosuccinate, [$(C_{18}H_{7}COOCH_{2})_{2}SO^{3-}Na^{+}$] in the emulsion polymerization.

They are widely used in many emulsion polymerization system, because of providing stabilization of latex particles by way of electrostatic repulsion mechanism. They also play a significant role to serve particle generations. Moreover, stabilized latex with anionic emulsifiers can be lose own stability via electrolytes adding and/or in freezing-thaw cycles. Moreover, stabilizing effectiveness of anionic emulsifiers is limited at high solid content emulsion polymerization (e.g.,> 40 %). In this situation, non-ionic emulsifiers should be preferred to surpass these stabilization problems. During the emulsion polymerization, non-ionic emulsifiers can provide nucleation and stabilization of latex particles.

2.4.2 Nonionic surfactants

Nonionic surfactants, which carry no charge unlike anionic or cationic surfactants, are amphiphilic compounds. Their lyophilic part does not seperate into ions. At the same time, there are nonionic, for instance such as tertiary amine oxides, which are able to gain a charge based on the pH value. For example, polyethers such as polyethylene oxides are protonated via acidic medium and exist in cationic form. Therefore, the more suitable definition of nonionic surfactants are carry no charge in the proponent working range of pH.

Alcohols, polyether, esters, or their combinations are widely known nonionic emulsifier type. The critical micellization concentration for such surfactants is generally much lower than that of the corresponding charged surfactants, and partly due to this, such surfactants are generally less irritant and better tolerated than the anionic and cationic surfactants.

Nonionic emulsifiers generally used to overcome the instability exhibited by ionic emulsifiers. Non-ionic emulsifiers can be preferred to surpass these stabilization problems. During the emulsion polymerization, it can provide stabilization of latex against electrolytes, water and high shear rates. In addition, it can be called as steric stabilization mechanism to preserve the interactive particle from coagulation and flocculation [18]. Consequently, for controlling the particle size distribution and providing the colloidal stability, anionic and nonionic emulsifiers are combined with each other in many emulsion polymerization recipes.

2.4.3 Cationic surfactants

A cationic surfactant is explained as when the molecules dissociate in solution, they give a surface-active caution and normal anion in solution. Cationic surfactants have a lower rate of use compared to anionic and nonionic surfactants. Nevertheless, worldwide production of cationic surfactants is exceeded 500.000 metric tons annually.

Cationic emulsifiers are used in specific applications where a positive charge on latex particles is desired. They are classified into the following major types: alkyl amines, ethoxylated amines, alkyl imidazolines, and quaternaries according to the chemical structures [19]. Hexadecyl trimethyl ammonium bromide and acetyl dimethyl benzyl ammonium chloride are quaternary salts, which can be used in emulsion polymerization as cationic emulsifiers.

2.4.4 Zwitterionic surfactants

A zwitterionic surfactants, the other name is amphoteric surfactant, has both anionic and cationic charge in their structure. The term of amphoteric is known to material, which demonstrates pH-dependent features. In addition, the structure of zwitterionic surfactant includes highly acidic and basic groups like as the quaternary ammonium group and the sulfonic group. Amphoteric emulsifiers demonstrate both anionic and cationic properties, respectively at high pH and low pH.

Alkyl amino or alkyl amino propionic acids are most known zwitterionic surfactants, generally these type surfactant not or rarely used in emulsion polymerization [20**]**.

2.5 Emulsion Polymerization of Vinyl Acetate

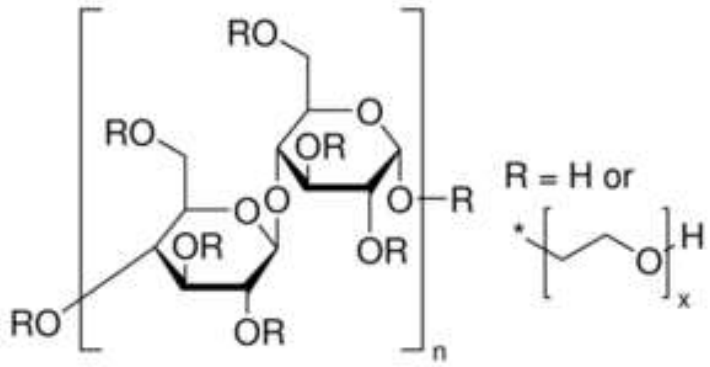
Emulsion polymerization of vinyl acetate (VAc) is generally used for architectural coating, adhesives, binder and another application. Useful combinations of durability and broad existance at low cost lead to use in this application.

Vinyl acetate polymerization is actualized by way of free-radical polymerization. Emulsion polymerization mechanisms of VAc vary from other vinyl type monomers such as butadiene and styrene. Smith-Ewarth Theory can explain emulsion polymerization mechanism properly. However, the VAc emulsion polymerization not suitable these theory. Compared to other hydrophobic monomers like a styrene, VAc monomers have high polarity and high reactivity. It is also high soluble in

water. For instance, VAc soluble in water approximately 2.5 % by weight, as this amount is $3.6x10^{-2}$ % by weight for styrene [21]. The high reactivity of the polymeric radical from VAc cause to high chain transfer to monomer and polymer. Therefore, it has a important effect on the polymerization rate, molecular structure, branching and the tendency toward graft copolymerization and gel fraction. Polyvinyl alcohol (PVOH) generally used as a protective colloids, which is the principal, surface-active agent. It affects branching and reaction route. Other important point in VAc emulsion polymerization is heat output. It is significant to removing of polymerization heat for the control of the polymerization reaction. Because exothermic reaction may cause destabilization, foaming and excessive boiling [22].

The delayed addition method in semi-continuous process is most widely used preparation method. Firstly, 5-15% of the VAc put into reaction medium with pre-emulsion solution which are contain emulsifier, water and initiator. After the particle formation, other ingredients are progressively added in the course of polymerization.

In VAc polymerization, generally persulphates are used as an initiator. Anionic and nonionic emulsifiers are usually preferred each other. In VAc emulsion polymerization, hydroxyl ethyl cellulose (HEC) and PVOH are used as protective colloids. Structure of HEC indicated below:



The optimum pH for VAc polymerization between 4.5-5.5. Therefore, sodium bicarbonate is preferred as buffer. Finally, an amorphous, non-crystalline, thermoplastic and soluble in alcohols, ketones and ethers polymers are obtained. PVAc is can be hydrolyze in the presence of water. After hydrolysis, acetic acid, vinyl alcohol units or acetate can be occurred. Mechanical properties, glass transition temperature (Tg), and minimum film formation temperature (MFFT) of PVAc are related to the their molecular weight. According to the several studies, the glass

transition temperatures of PVAc having an avarege molecular weigth is 30 C^o. MFFT value is nearly 20 C^o and tensile strength between 29.4-49.0 N/mm^2 ,their Young modulus is approximately 600 N/mm^2 at 25 C^o, and elongation at break value between 10-20% at 20 C^o [20]. In addition, PVAc is degredated above the 150-200 C^o and it show brittle properties below the 15-20 C^o. All of the mentioned properties, not only depend on molecular weights, but also based on the ingredients, types of emulsion polymerization etc.

2.6 Acrylic Emulsion Polymerization

Thanks to the adhesion, improved flexibility and their moderate cost compared to phenolic, styrene-butadiene latex, and polyvinyl acetate emulsions, acrylic polymers have acquired a strong presence in coatings and allied industries [36]. Nevertheless, acrylic latexes, which improve light stability, outdoor durability, hardness, gloss reduction and chalking, they have to be used in various applications.

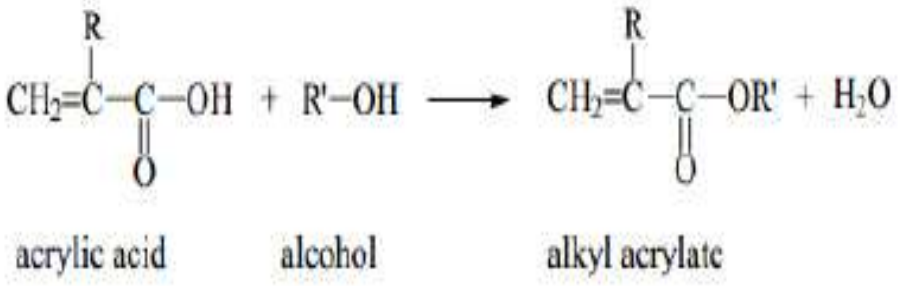
Acrylics can be form as solid beads, solution polymers, and emulsions. The most produced form is emulsion form in use. Compared to the solid and solution polymers these provide the lower manufacturing costs and hazards.

Homopolymers latexes of major monomers possess in a multitude of application areas such as coating, textile, paint, construction, leather etc. These polymers have stable, durable, have good pigment binding capacity, impact resistance, chemical resistance. The ratio of their monomers an array of polymers with a large number of glass transition temperatures could be generated with emulsion polymerization method by diversifying and a great number of copolymers could be generated [23-25].

Throughout the emulsion polymerization process the water which is used as the locus to disperse and wet the micelles behaves as a solvent for the surfactants and initiators alongside a heat transfer locus [25,26,35].

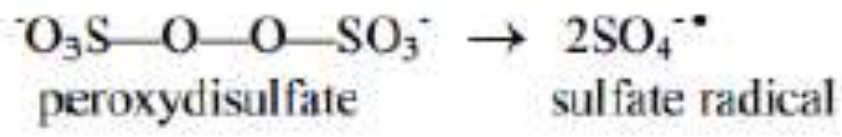
Acrylic monomers obtain from esters of acrylic and methacrylic acid. It can give as example several esters, can include hydroxyl groups (e.g., hydroxyethyl methacrylate), functional groups such as amino groups (e.g., dimethylaminoethyl methacrylate), amide groups (acrylamide) including the carboxylic acid functionality of the unesterified monomer, which are ethyl, isobutyl, methyl, 2-ethylhexyl,n-butyl,

octyl, lauryl, and stearyl. Acrylic monomers could be multifunctional. A reversible reaction which prepare the monomers between an acrylic acid and an alcohol. This reversible reaction indicated below:

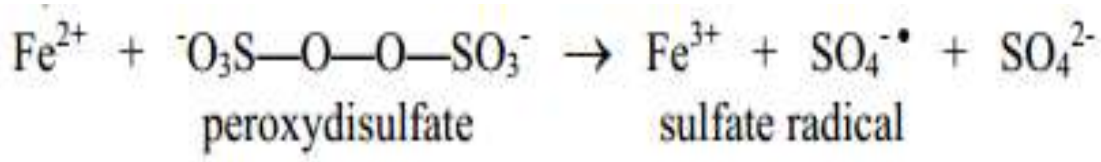


The major monomers, which widely used are methyl methacrylate, ethyl acrylate and butyl acrylate, alongside non-acrylic monomers, which are given the example as vinyl acetate and styrene acting in the same way.

The initiators (catalysts) that are largely used are water-soluble peroxidic salts that are given examples as ammonium or sodium peroxydisulfate. The reaction could be started by thermal initiation or it can be began redox initiation. The reaction is that the peroxydisulfate dissociates to give two SO^{4-} radicals in thermal initiation as shown below:



A reducing agent (generally Fe2+ or Ag+) is used to ensure one electron in redox initiation is that it brings about the peroxydisulfate to dissociate into a sulfate radical and a sulfate ion.



Straight acrylics that are polymer dispersions particularly consisted of acrylate and/or methacrylate monomers. For both types of copolymer, they have a great number of monomers. These monomers exceedingly show an alteration in respect to glass transition temperature and the polarity of the homopolymers, which are prepared

from them. Table 2.1 indicates some monomer's water solubility and Tg values. As far as application conditions are concerned, monomer composition is determined indicate. Polyacrylates and polymethacrylates that give justification their relatively high price have the particular features. These features are the generally very good weatherability and UV stability, good water resistance, high transparency, yellowing resistance, great convenience of distinctness in toughness, hardness and flexibility.

Table 2.1 : Water solubility's and glass transition temperatures of principle monomer.

Monomer	Water solubility's at 25°C in g/100 cm^3	Tg of the homopolymers 25°C
Methyl acrylate (MA)	5.20	22
Ethyl acrylate (EA)	1.60	-8
n-Butyl acrylate (BA)	0.15	-43
Methyl methacrylate (MMA)	1.50	105
n-Butyl methacrylate (nBMA)	0.08	32
Styrene	0.02	107
Acrylonitrile	8.30	105
Vinyl acetate	2.40	42

Acrylic resins, which are comprise chief esters of acrylic acids or methacrylic acid usually used in paint and coating industries. They could be used in textile, adhesive, printing inks, paper coating and construction industries as well. Amount of acrylic esters and methacrylic esters, which have rather diversified properties in polymer, indicate material properties, hardness, chemical resistance, flexibility, leveling along film formation [27]. The reactivity of their double bonds differentiates esters of acrylic acid or methacrylic acid. After initiation, polymerization happens via the association of radicalic monomers and free monomers, which are ion esters of acrylic and methacrylic acid. Esters of ion acrylic acid and methacrylic acid, which act as building blocks for polymers, are called monomers. Further building blocks capable of forming polymers conjunction with acrylic and methacrylic esters are called comonomers [28].

Water-borne acrylic dispersions are generally prepared by emulsion polymerization. Compared to solution polymerization emulsion polymerization has more advantages such as, synthesis of high molecular weight polymers can be possible. High solid content (50% or higher), low viscosity polymers can be produced with emulsion polymerization.

2.7 Emulsion Copolymerization

Generally, latexes are consisted of two or more monomer. In copolymerization, two or more monomers are associated into the polymer chains. The copolymer chains are generated by simultaneous polymerization, which have two or more monomers in emulsion. Emulsion copolymerization permits the production of materials with properties, which could not be attained by latex products, that is, homopolymer latexes, or by blending homopolymers. Generally, the features of the materials, which are required, are impressed by the market. Currently most of the materials features are accomplished by combination of more than two monomers in the copolymer product.

Typical industrial emulsion polymerization formulations are mixtures of monomers, which are given hard polymers, and monomers, which are resulted in soft polymers.

Styrene and methyl methacrylate could give an example to monomers, which are given hard polymers that have a high glass transition temperature; Tg. Soft polymers have a low Tg. For instance, ıt formed from n-butyl acrylate. The industrial emulsion polymerization formulations include small amounts of functional monomers, which are given an example as acrylic and methacrylic acid to impart developed or special characteristics to the latex product as well. Take in consideration that the colloidal stability of the latex product could be acutely developed by acrylic and methacrylic acid. Moreover, some applications might request the addition of other specialty monomers. These monomers make the kinetics of the copolymerization even more complex.

Huge amounts of polymers, which are produced by emulsion polymerization, are copolymers in that the features of the individual polymers could be synergistically raised by the generation of copolymers.

However, it is always complicated to predict that the final composition of the copolymer chains will be the same as the starting monomer ratios, since different monomers have different reactivity's in a given system. To propose this, the more reactive monomer may be previously polymerized, since reactivity's are different from each other so that it forms the core of the extruded particles in this polymer and then forms an outer cover of the richer particles in less reactive monomers. This leads to different monomer concentration on these particles. Similarly, there may be

2.8 High Solid Content Emulsion Polymerization

2.8.1 Introduction

Over the million tones, different latexes are manufactured every year in the World. Because of having miscellaneous properties, latexes use a wide range of area such as textiles, paper paints, floor polish, adhesives, coatings and make-up [29-34]. High solid content (HSC) latexes are described as having more than 60% solid content. Compared to traditionally latexes which have 40-50% solid, high solid content latexes have distinguished properties due to advantages such as maxizing the production, minimizing the energy consumption, transportation cost and storage capacity, providing flexible last product formulation, decreasing the film-forming time and developing surface coverage.

As the emulsion solid content increases, the latex viscosity increases sharply. Therefore, heat removal rate, mass transfer, mixing and latex stability can be affected by raised viscosity. It is most important factor that is particle size distribution (PSD) and colloids particle size for controlling of viscosity.

Rheological behavior is always a limiting factor present in the preparation process. The viscosity is a function of the viscosity of the aqueous phase and the packing factor and the volume fraction. It can be described as Mooney Equation (2):

$$\ln \eta = \ln \eta_K + (K_F * V_D / 1-(V_D / K_P)) \quad (2)$$

where η = viscosity, η_K= viscosity of the aqueous phase, K_F=form factor (2.5 for spherical particles), V_D= volume fraction of disperse phase, and K_P= packing factor (0.637 for monodisperse, close- packed spheres).

When the volume fraction is close to the packing factor, then the viscosity increases directly [37]. Effect of particle size distribution on relative viscosity is shown in Figure 2.5. If particle diameter diminishes, the raise in viscosity falls within at lower and lower volume fraction of the polymer, because of increasing particle interaction and packing density. It is indicated that particle size of latex of 100 to 200 nm retain their fluidity for solid contents of 50 up to maximum of 55% by weight [10]. Bimodal or multimodal particle size distribution is necessary for preparing solid contents of more than %60 by weight.

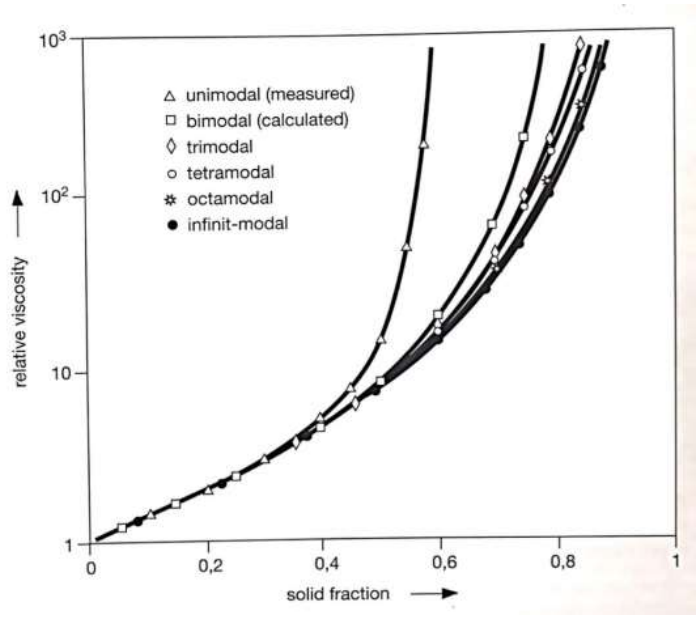


Figure 2. 5 : Relationship of solid fraction, particle size distribution and viscosity [37]

2.8.2 Preperation method

Many research groups have attained HSC latex via several technique last years. Preperation of high solid content and considerable viscosity latexes are provided by four techniques. Although there are four main methods, which are conventional emulsion polymerization, miniemulsion polymerization, self-emulsification polymerization and concentrated emulsion polymerization, generally conventional and semi-continuous emulsion polymerization are preferred in acrylic emulsion polymerization.

2.8.2.1 Conventional emulsion polymerization

Blending

High solid content bimodal and trimodal latexes can be prepared via mixing monomodal latex, which has different particle size. After distillation and permeation, it is essential to remove extra water from medium due to raising the solid content. Compared to other preparing technology, it has considerable advantages such as simple procedure, suitable and quantitative control. According to the many scholars, there are the relations between particle size distribution (PSD), apparent viscosity (η), the volume fraction (ϕ), and maximum volume fraction (ϕ max). This parameter provide to information to preparing high solid content-low viscosity latexes [32].

On the other hand, monomodal latexes, which are produced industrially, have less than 60% solid content. In addition, when the latexes, which are desired to be produced particle, size decreases, solid content decreases. The high solid content latexes obtained by physically blending of two or more monomodal latexes, always less than 60% solid content in each case. To obtaining more than 60% solid content, evaporation is needed to remove of redundant water. The latex stability can deformed throughout the evaporation of water. In addition, coagulation or flocculation can happen. Moreover, this method is not economical from the view of indusrial. According to the this approach, small particles must be among 4 and 10 times smaller than the large particles and volume fraction of small particles should be in the ratio of 15-20% [29].

2.8.2.2 Semi-continuous emulsion polymerization

Semi-continuous emulsion polymerization drawn much interest for preparing HSC latexes in last years. Controlling of particle size distribution is provided by semi-continuous emulsion polymerization therefore, this method is widely used in industry. The best way to produce multisized particle size distribution latex is semi-continuous emulsion polymerization. It may be categorized into three class: Adding Surfactant, Adding Seed Emulsion, Adding Surfactant+Seed, according to the preparation method. Depending on the in situ nucleation, bimodal or trimodal dispersed HSC latex can produced by semi-continuous emulsion polymerization. Schematic representation of producing bi- or trimodal high-solid content latex is showed in Fig.2.6 .

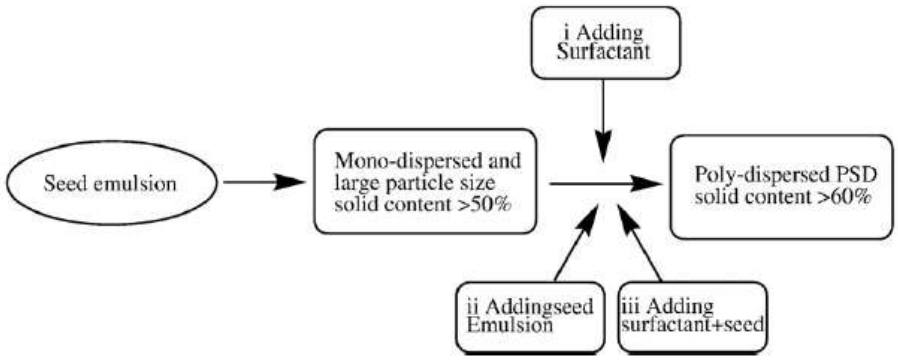


Figure 2.6: Producing of bimodal or trimodal high solid content latex via semi-continuous emulsion polymerization

Injection of additional surfactant

This preparation method includes two steps. In the first instance, a determined amount of mono-dispersed emulsion that has large particle is generated. After that, an amount of additional surfactant is added along the semi-batch emulsion polymerization. Consequently, bimodal and trimodal PSD polymer latex can be attained. Earlier publications indicated that anionic emulsifier considered appropriate the production of small particles, and the features and amount of the additional surfactant, besides the addition moment, far better affected the secondary-generated particles. In the spite of its excessively irreproducible results or crucial stability problems, this process type was generally difficult to dominate several research findings are continued to use published in up-to-date works .A second crop of small major particles was initiated by the injection of sodium dodecyl sulfate (SDS) into the reaction locus beneath monomer-starved conditions, and a bimodal PSD was generated via Min and Gostin in 1979 [32].

Injection of intermediate seed

Injection of intermediate seed is other method to produce HSC latexes. After producing of large particles small amount of seed was suddenly added in reactor. This method is showed at Fig.2.7.

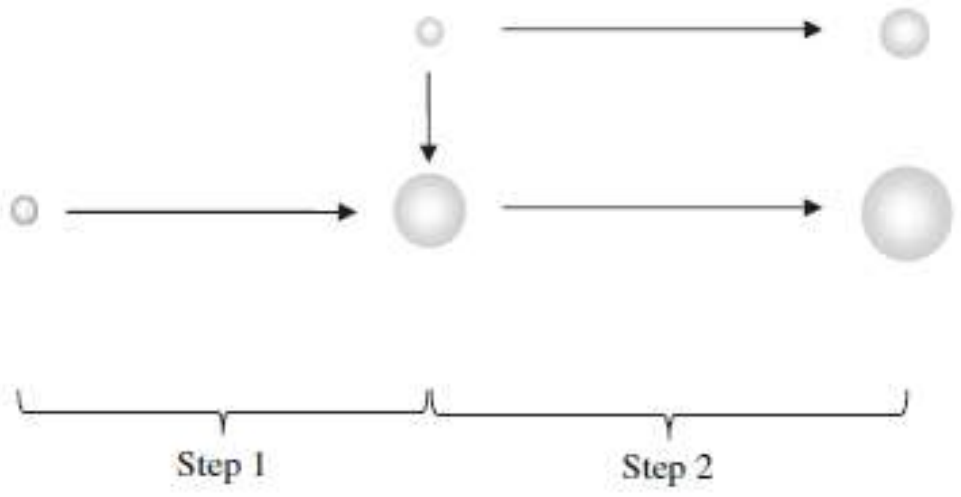


Figure 2.7: Schematic representation of injection of intermediate seed

Chu et al. produce the first bimodal polymer latexes via adding small amount of other seed through the semi-continuous emulsion. The seed emulsion was monomodal latex, solid content 50% weight and diameter at 75 nm. In seeded emulsion polymerization, PSD can control magnificently. According to the Chu et al., two-stage seeded emulsion polymerization provides good particle size distribution. The first step of semi-continuous emulsion polymerization 60% monomer emulsion is consumed, after adding seed emulsion remained monomer emulsion is feeded. It is indicated that small particles grew more than large particles, but growing is limited [33].

Maximum particle diameters below 350 nm and solids content 70wt% bimodal PSD latexes are synthesized by Mariz et al.. In this article, an iterative strategy is used for producing optimum PSD latexes. Optimum bimodal PSD is calculated by theorically and then, it was attained by experimentally.

Firstly, small amount of seed emulsion was added in reactor and feeded with monomer emulsion via monomer-starved conditions, till a theorically calculated particle size. Then, certain amount of seed was added again directly. Finally, coagulum-free, bimodal PSD latex is obtained. (%70 weight of solid content and particle size below the 350 nm) [30].

Injection of seed and additional surfactant

Another method is that injection of seed and additional surfactant for producing bimodal or trimodal HSC latexes. According to the Chu et al., secondary seed and surfactant was added in a reactor directly. Emulsion polymerizations consist of two step. Firstly, initial seed was prepared in a reactor, and secondly, seed emulsion, surfactant and initiator were added [33]. Trimodal dispersed HSC latexes is attained. The large particles were from the growth of initial colloid. The intermediate paticles came from the growth of secondary seed, and lastly the small ones are happened by adding surfactant via renucleation.In the presence of high amount of hydrophilic monomer, Schneider and their group prepared trimodal dispersed HSC latexes via adding seed and surfactant in reactors. Polymerization is separate to two steps. Firstly, different size monomodal seed latexes with a 50% solid content is prepared. Particle sizes of these seeds are 500 nm and 250 nm [34]. However, ingredients of pre-emulsion not contain any anionic surfactant to decrease the probability of renucleation. Schematic representation of trimodal dispersed HSC latexes is showed

at Fig.2.8. Finally, trimodal dispersed latexes, which have 65% solid content by weight obtained. The viscosity of trimodal latexes are approximately 2500 mPa s^{-1} when shear rate at $20s^{-1}$.

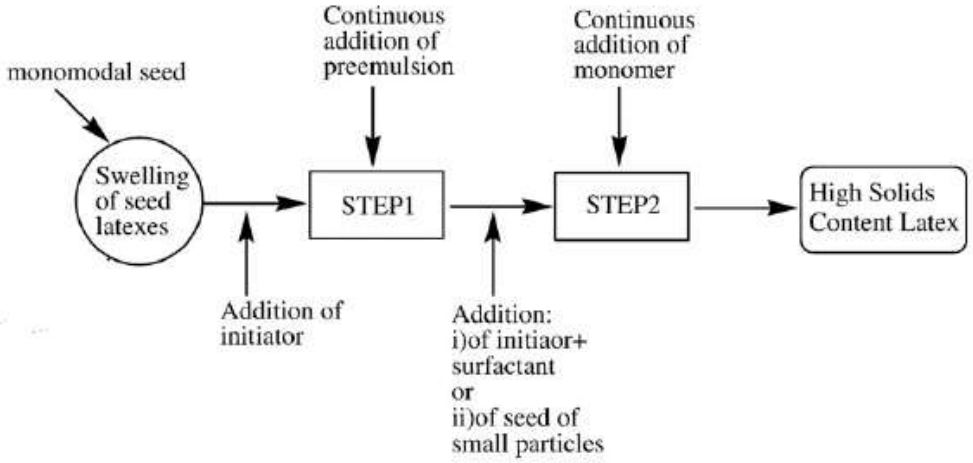


Figure 2.8 : Trimodal HSC latexes prepared by Schneider et al. [32]

3. EXPERIMENTAL PART

3.1 Materials

Butyl acrylate (BA) (Aldrich), Methyl methacrylate (MMA) (Merck), Methacrylic acid (MAA) (Merck), Vinyl acetate (VAc) (Aldrich), Potassium persulfate (Aldrich), toluene diizocyanate (TDI) (Aldrich) , poly(ethylene glycol) dimethyl ether (MPEG 500)(Mn 550) (Aldrich), Dimetyl formamide (DMF) (Aldrich), Dibutyltin dilaurate (DBTDL) (Aldrich), sodium bicarbonate (Aldrich) , Dowfax 2A1 (Dow Chemical), Liropon SLS , t-BHP solution %70 in water (Sigma-Aldrich), Acticide FS(N) (Thor), THF for chromatography analysis (Merck) were analytical grade chemicals .

3.2 Instruments

Particle Size Distribution measurement: Particle size distributions and the average particle sizes were measured by laser scattering using Malvern Nano ZS Zetasizer instrument. The measurements were carried out at 25°C in deionizes water. All emulsion polymers are diluted with a thousand times with deionizes water.

Glass transition temperature measurement: The glass transition temperatures of the copolymer were measured by using a Perkin Elmer DSC 6000 instrument at a heating rate of 10°Cmin -1.

Latex viscosity: The PVAc and Poly (BA co-MMA) latex viscosities were measured by using Brookfield Viscometer DV-III Model Programmable Rheometer at 20°C at 250 rpm and 330 1/s shear rate. High solid content latexes were measured by using Brookfield LV Model instrument with Spindle no. 2,3 and 4 at 20 rpm at 20°C.

Gel permeation chromatography measurement: Gel permeation chromatography (GPC) traces were taken by using TOSOH EcoSEC GPC/SEC series consisting of a pump, a RI detector, LS detector, IR detector and TSK gel liquid chromatography columns. Tetrahydrofuran was used as the eluent, and the flow rate was 1 mL/min.

Surface tension measurement: Surface tension of emulsion copolymers are measured by Attension by KSV Instrument via ring method.

FT-IR measurements: Polyurethane based surfactant was analysed by using a Thermo Scientific Nicolet instruments at 25 °C.

3.3 Synthesis of Urethane Containing Polymeric Surfactant

20 g (0.040 mole) of methoxy poly(ethylene glycol) (MPEG 500) was dissolved in 25 mL of DMF. 3.48 mL (0.020 mole) of TDI and catalytic amount of DBTL were added to the reaction mixture at room temperature and then the reaction was proceeded at 60±2 ^{0}C for 24 h.

Then, yellow viscose liquid product was obtained and poured 100 mL of hexane to precipitate the surfactant.

The obtained polymeric surfactant was characterized by using FT-IR spectroscopy, GPC, critical micelle measurements.

3.3.1 Emulsion polymerization of vinyl acetate and MMA-co-BU with polyurethane based surfactant

Polymerization reactions were performed by using batch emulsion polymerization technique depending on surfactant concentration and time.

The polymerizations were performed at 70±2°C for VAc and at 80±2°C for MMA-co-BA polymerizations. The recipts of PVAc and PMMA-co-BA polymerization conditions were given in Table 3.1. and Table 3.2 respectively.

Particle size of latexes was determined by Zetasizer Nano ZS and other characterizations of the latexes were performed with surface tension and viscosity measurements.

Polymers were precipitated by adding NaCl and filtered. Then obtained PVAc polymers were washed with excess of hot water and methanol and were dried under vacuum at room temperature for 24 h.

Molecular weights of the polymers were determined by GPC measurements.

Table 3.1 : Recipe for the emulsion polymerization of VAc using the polymeric surfactant

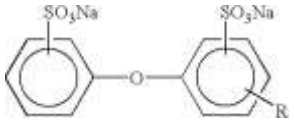
	1	2	3	4	5
VAc (mL)	5	5	5	5	5
Surfactant (g)	0,2	0,12	0,062	0,12	0,062
KPS(g)	0,1	0,1	0,1	0,1	0,1
DI Water (mL)	50	50	50	50	50
Reaction Time(min)	105	105	105	60	60

Table 3.2: Recipe for the emulsion polymerization of MMA/BA using the polymeric surfactant

	1	2	3	4
BA (mL)	2,8	2,8	2,8	2,8
MMA (mL)	2,1	2,1	2,1	2,1
Surfactant (g)	0,1	0,22	0,1	0,2
KPS (g)	0,1	0,1	0,1	0,1
DI Water (mL)	50	50	50	50
Reaction Time (min)	150	150	240	240

3.2.2 Emulsion polymerization of VAc with Dowfax 2A1

Polymerization reactions were performed by using batch emulsion polymerization technique depending on Dowfax 2A1 (alkyldiphenyloxide disulfonate) concentration and time (Scheme 3.1).



Scheme 3. 1: Chemical structure of Dowfax 2A1

The polymerizations were performed at 70±2°C for VAc polymerizations. The recipt of the polymerization conditions were given in Table 3.3.

Table 3.3 : Recipe for the emulsion polymerization of VAc using the commercial surfactant Dowfax 2A1

	1	2	3	4	5
VAc (mL)	5	5	5	5	5
Surfactant (g)	0,2	0,12	0,062	0,12	0,062
KPS (g)	0,1	0,1	0,1	0,1	0,1
DI Water (mL)	50	50	50	50	50
Reaction Time (min)	105	105	105	60	60

Particle size of latexes were determined by Zetasizer Nano ZS and other characterizations of the latexes were performed with surface tension and viscosity measurements. Polymers were precipitated by adding NaCl and filtered. Then obtained PVAc polymers were washed with excess of hot water and methanol respectively. Polymers were dried under vacuum at room temperature for 24 h. Molecular weight of the polymers were determined by GPC measurements.

3.3 Seed Latex Synthesis of Poly(MMA-co-BA)

Table 3.4 : A typical seed formulation

	Ingredients	wt (%)
	DI Water	57.49
	SLS	1.60
	Sodium Bicarbonate	0.02
	Sodium metabisulphite	0.02
	Ammonium persulphate	0.15
Feed 1	Sodium metabisulphite	0.01
	DI Water	0.30
Feed 2	Butyl acrylate	19.30
	Methyl methacrylate	19.30
	t-BHP	0.01
	Biocide	0.10

According to the literature, monomodal dispersions which particle size 30 to 80 nm are fluid up to solid contents of 35 or 45% by weight [10]. Therefore, 40% by weight seed latex was prepared by semi continuous emulsion polymerization in a glass reactor. The reaction medium was purged with nitrogen and subsequently heated to 60^0C in a thermostated water bath under stirring at 200 rpm during the reaction. The typical seed formulation was given in Table 3.4. Firstly, water, surfactant (SLS) and buffer (sodium bicarbonate) were added into the reactor and then heated up to 60 ± 2^0C. Then, ammonium persulfate and sodium metabisulphite were added into the reaction vessel respectively as a redox couple. Monomer mixture and ammonium persulfate solution are fed into the reactor vessel separately during 3 hours.

The polymerization reaction was proceeded for 1 hour at these conditions. At the end of the polymerization, t-BHP was added into system to polymerize of the free monomers in reaction medium. Then, the final product was cooled until the room temperature gradually and the biocide was added under 50 0C. Obtained seed latex

has 40 wt% solids content, 42.71 nm of the average size and 0.108 of PDI value. All detailed of seed latex data were given at Appendix B.

3.3.1 Seeded high solid content poly(MMA/BA/MAA) latex synthesis

Two different methods were used to produce high solid content emulsion polymerization. Firstly, the polymerization was carried out in 2L glass reactor at 80 ± 2^{0}C and 200 rpm stirring rate. The required amount of seed polymer, a small amount of monomers and water were added into reactor. When the desired temperature was reached, the feeding of initiator and pre-emulsion were started at constant feeding rate separately. After that, a certain amount of seed was introduced into the reactor shot wise in the second hour of feeding, keeping the feeding of water, monomers, surfactant and ammonia to reach the desired solids content. After about 180 minutes of feeding, the reaction was proceeded for 1 h in batch. The same polymerization reaction was also carried out with different amount of seed content. Reactions were repeated with as solid ratios of 60% and 65%. The typical polymerization receipt was given in Table 3.5

Table 3.5 : Seeded high solid emulsion polymerization formulation (60% SC)

	Ingredients	Part of weight
	DI Water	14.00
	Seed	0.740
	Butyl acrylate	0.050
	Methyl methacrylate	0.050
Feed 1	DI Water	3.000
	Ammonium per sulphate	0.150
Feed 2	DI Water	16.810
	Surfactant	0.750
	Butyl Acrylate	27.910
	Methyl methacrylate	27.910
	Methacrylic acid	0.690
	Ammonia	0.500
2nd hour of feeding	Seed	3.675 , 7.35 , 11.00
	Biocide	0.100

3.3.2 Unseeded high solid content poly(MMA/BA/MAA) latex synthesis

Secondly, the polymerization was carried out in 2 L reactor at 80 °C and 200 rpm stirring rate. Water and small amount of monomer were added in the reactor during reaction. After reaching the desired temperature, the initiator and pre-emulsion solution (water, monomers, surfactant and ammonia) were drop wisely added into the reactor to start the polymerization. After 2 hours, a certain amount of seed was put into the reactor shot wise, keeping the feeding to reach the desired solids content. Feeding was finished within 180 hours. Then, the reaction mixture was left to react for 1 h in batch. The polymerization was repeated with increasing and decreasing the half-and-half amount of seed during the feeding is continuing. Reactions were also performed with desired solid ratios of 60% and 65%. The receipt was given in Table 3.6

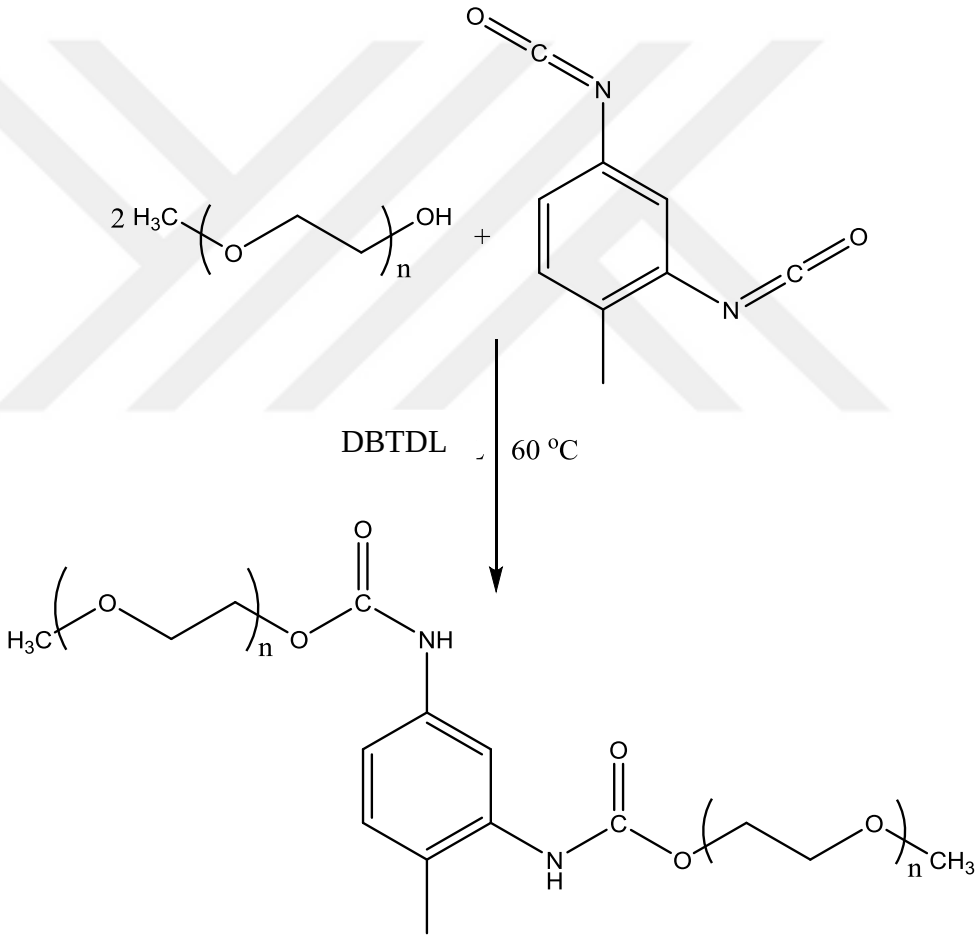
Table 3.6: Unseeded high solid emulsion polymerization formulation (60% SC)

	Ingredients	Part of weight
	DI Water	14.00
	Butyl acrylate	0.050
	Methyl methacrylate	0.050
Feed 1	DI Water	3.000
	Ammonium per sulphate	0.150
Feed 2	DI Water	16.810
	Surfactant	0.750
	Butyl Acrylate	28.06
	Methyl methacrylate	28.06
	Methacrylic acid	0.690
	Ammonia	0.500
2nd hour of feeding	Seed	3.675 , 7.35 , 11.00
	Biocide	0.100

4. RESULTS AND DISCUSSION

4.1.Synthesis and Characterization of Surfactant

In this study, the new polyurethane based surfactant (PU) was synthesized starting reaction between MPEG-500 and TDI in the presence of DBTDL as catalyst and DMF as solvent at 60^0C (Scheme 1).



Scheme 4. 1 Chemical representation of polyurethane based surfactant

Molecular weights of surfactant was determined by GPC and Mn and Mw values were found as 1100 Da, 1354 Da respectively. These result show that chain extension was occurred after urethane formation. In addition, chemical characterization of the surfactant was carried out by FTIR and H-NMR. According to the FTIR spectra (Fig 4.1), characteristic urethane carbonyl peak and C=C aromatic vibration peaks were

observed at 1723 and 1600 cm^{-1} respectively. The bending and C-N stretching vibration peaks appear at about 1535 $cm^{-1}$and 1228 cm^{-1}.The N-H vibration peaks were observed at 3400 cm^{-1}. N-H vibration peaks were observed between 3000-3500 cm^{-1}.

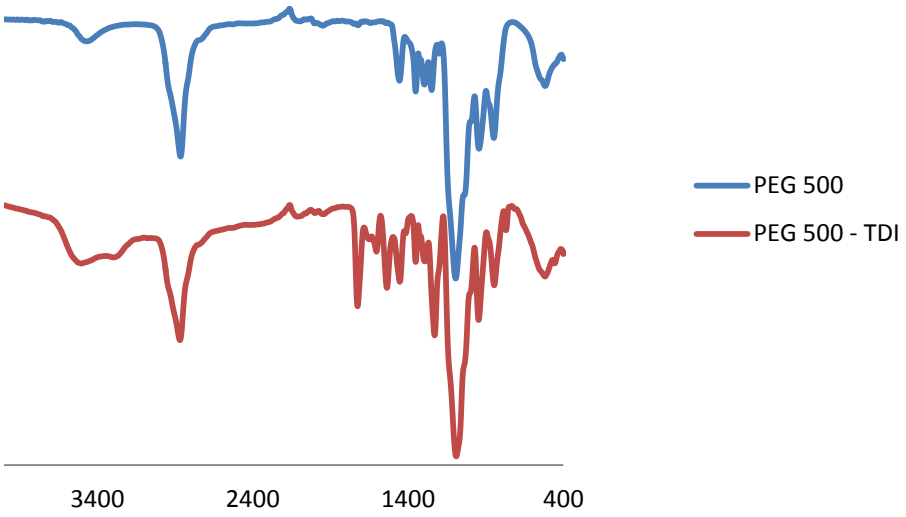


Figure 4. 1: FT-IR spectra of PU based surfactant and PEG500

4.2. Determination Critical Micelle Concentration (CMC) of the PU Surfactant

CMC value was determined by using du Nouy tensiometer. Surface tension vs surfactant concentration was ploted and CMC value was calculated as 0.68 mg/mL at 25°C (Fig 4.1)

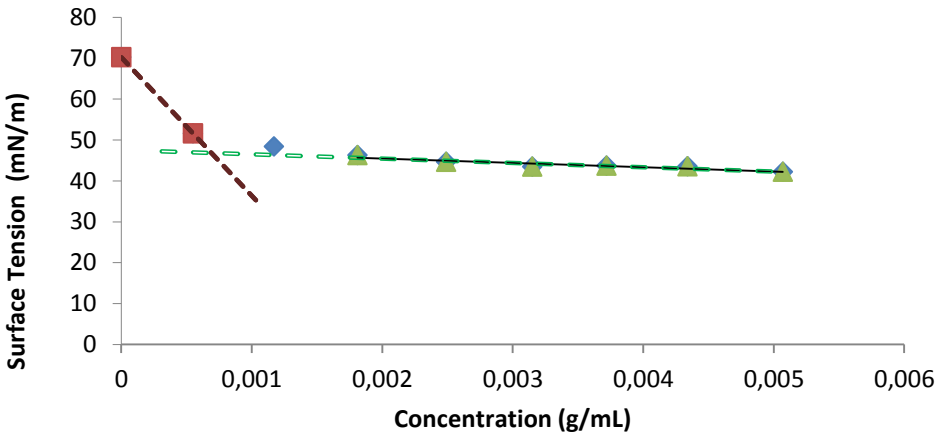


Figure 4. 2: CMC of PU based surfactant

4.3 Emulsion Polymerization of VAc

In this study, VAc was polymerized by emulsion polymerization technique using potassium persulfate as initiatior and PU based surfactant and Dowfax 2A1® as surfactants, respectively and used them in emulsion polymerization of VAc homopolymerization and MMA-co-BA copolymerization. PU is a non-ionic surfactant and Dowfax 2A1 has anionic structure. Therefore, polymer latex properties of VAc was compared depending on surfactant type, surfactant quantity and polymerization time (Table 4.1).

Table 4.1 : VAc emulsion polymerization results

a)Reaction Time : 105 minute b).Reaction Time : 60 minute

Surfactant Quantity (g)	Viscosity (cP)	Particle Size (nm)	Surface Tension (mN/m)	M_n	Viscosity (cP)	Particle Size (nm)	Surface Tension (mN/m)	M_n
	PU Surfactant				**Dowfax 2A1**			
0.06	1.67	313	55.72	51254	1.57	106	50.71	134492
0.12	1.58	197	55.40	54482	1.50	79	45.81	482694
0.20	1.57	145	54.70	98149	1.52	70	43.15	16781571

b)

Surfactant Quantity (g)	Viscosity (cP)	Particle Size (nm)	Surface Tension (mN/m)	M_n	Viscosity (cP)	Particle Size (nm)	Surface Tension (mN/m)	M_n
	PU Surfactant				**Dowfax 2A1**			
0.06	1.48	220	55.45	62958	1.74	98	53.15	913427
0.12	1.58	195	55.21	59850	1.64	91	48.64	277971

Characterization of latexes was performed by Brookfield viscometer (Fig. 4.3), surface tension, particle size and Mn measurements.

Surface tension of PVAc latexes obtained by PU surfactant are higher than the prepared Dowfax 2A1, and do not change very seriously depending on surfactant quantity, and reaction time. Otherwise PVAc latexes by using Dowfax 2A1, increasing of surfactant quantity and reaction time surface tension of latexes decrease. Particle size distrubition of the latexes was examined by Malvern Zeta Sizer Nano ZS.

According to Table 4.1. both latexes which is obtained using PU and Dowfax 2A1, increasing the surfactant concentration, particle size decreases. It can be explained a greater number of surfactant molecules emigrating from the oil phase to the aqueous phase of the emulsion and small size droplets would be produced. Also, small particle size latexes were obtained by using anionic surfactant.

According to the literature, when the polar groups are introduced to the chain units, the surface tension of polymer latex increases due to the stronger van der Waals forces between the macromolecules [38].

Figure 4. 3: Brookfield Viscosimeter

4.4 Characterization of MMA/BA Emulsion Polymers

Table 4.2 : MMA/BA emulsion polymerization results

a) Reaction Time : 150 minute b) Reaction Time : 240 minute

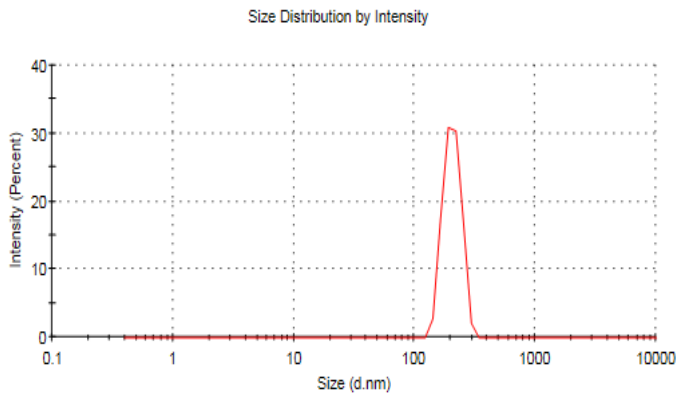
a)

Surfactant Quantity (g)	Viscosity (cP)	Particle Size (nm)	Surface Tension (mN/m)	M_n
0.10	1.50	206*	60.44	94658
0.22	1.56	209 and 643**	57.83	54814

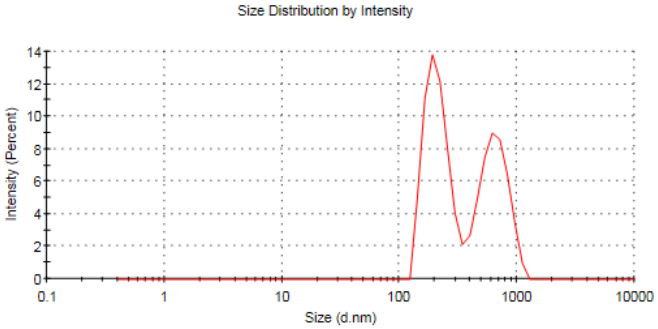
b)

Surfactant Quantity (g)	Viscosity (cP)	Particle Size (nm)	Surface Tension (mN/m)	M_n
0.10	1.52	218*	60.60	93166
0.20	1.48	213 and 544**	59.15	51254

* Monomodal paticle size distribution **Bimodal particle size distribution



(a)



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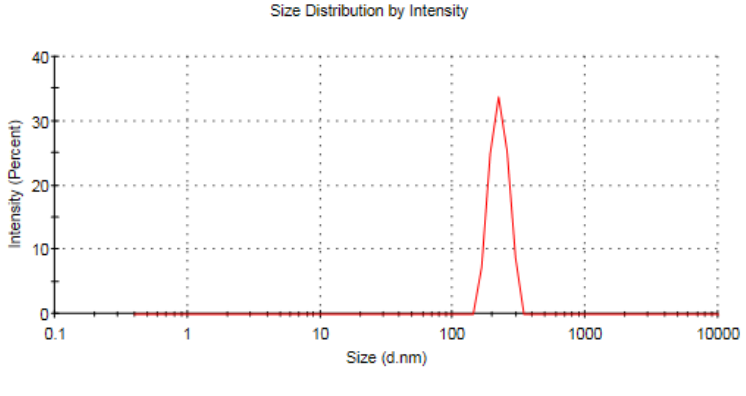
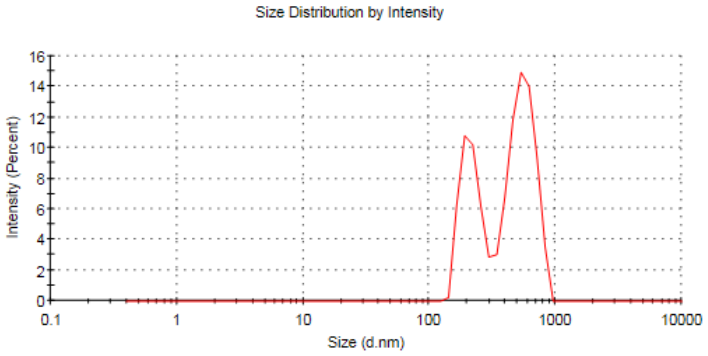


(c)



(d)

Figure 4. 4: Particle size distrubution of Poly(MMA-co-BA) Which synthesized by different amount PEG500-TDI surfactant 0.1 g surfactant, 150 minute, (b) 0.2 g surfactant, 150 minute (c) 0.2 g surfactant, 240 minute, (d) 0.2 g surfactant, 240 minute

Emulsion copolymerization of MMA-BA by using PU surfactant was performed depending on surfactant quantity and time. Solid content of the latex was determined about 9-12 % percentage. Therefore, viscosities are not high and surface tensions are not different. Particle size (Fig 4.4) changes depending on the surfactant concentration and increasing surfactant quantity bimodal distribution was also observed besides the monomodel. According to the literature, particle size can also increase by coalescence with other particles, either because of insufficient stabilization by surfactants or due to the shear stress imparted on the particles by the mixing in the polymerization system [41,42].

4.5 High Solid Content Emulsion Polymerization Characterization

Twelve different acrylic emulsions, which have high solid content (60% and 65%), are synthesized by seeded emulsion polymerization. Emulsion copolymers are shown in Fig 4.5. The characteristic of polymerization and the solid content of the emulsion polymers are given in Table 4.3.

The solid content quantity was calculated as follows:

$$\text{Solid\%} = [\, Wf \,/\, Ws \,] \qquad (1)$$

where Wf and Ws are weights of dried emulsion and emulsion, respectively.

Table 4.3 : Solid content of P(MMA/BA) emulsion polymerization results

Predicted Solid Content (%wt)	Seed in the reactor (%wt)	Seed added at 2nd hour (%wt)	Calculated Solid Content (%wt)
60.00	0.74	3.68	59.20
60.00	0.74	7.35	60.00
60.00	0.74	11.00	60.00
60.00	0.00	3.68	60.50
60.00	0.00	7.35	60.00
60.00	0.00	11.00	59.90
65.00	0.74	3.68	65.50
65.00	0.74	7.35	65.00
65.00	0.74	11.00	65.50
65.00	0.00	3.68	64.70
65.00	0.00	7.35	65.20
65.00	0.00	11.00	65.09

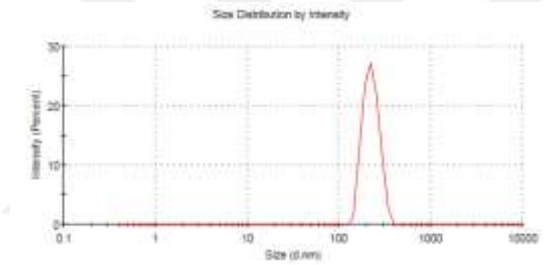
Figure 4. 5: Emulsion copolymers

Average particle size of the copolymers and their distributions are shown in Table 4.4 particle size distribution graphs are given Figure 4.3, Figure 4.4 , Figure 4.5 and, Figure 4.6.

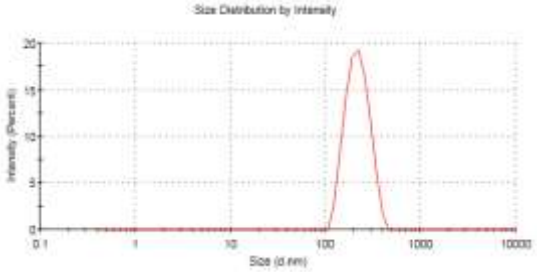
Table 4.4 : Avarage particle size and particle size distribution of emulsion polymers

Predicted Solid Content (%wt)	Seed in the reactor (%wt)	Seed added at 2nd hour (%wt)	Particle Size Distribution	Particle Size (nm)	
				Small Particle	Large Particle
60.00	0.74	3.68	Monomodal	-	225
60.00	0.74	7.35	Monomodal	-	209
60.00	0.74	11.00	Monomodal	-	205
65.00	0.74	3.68	Monomodal	-	220
65.00	0.74	7.35	Monomodal	-	226
65.00	0.74	11.00	Monomodal	-	221
60.00	0.00	3.68	Bimodal	77	679
60.00	0.00	7.35	Bimodal	75	632
60.00	6.00	11.00	Bimodal	59	598
65.00	0.00	3.68	Bimodal	80	699
65.00	0.00	7.35	Bimodal	102	851
65.00	0.00	11.00	Bimodal	173	985

(a)



(b)



(c)

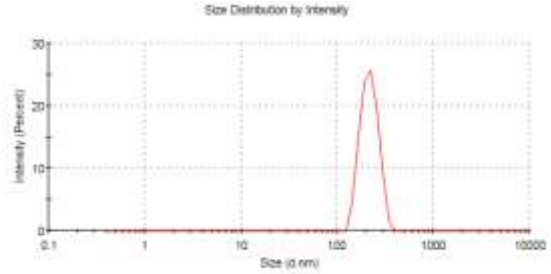
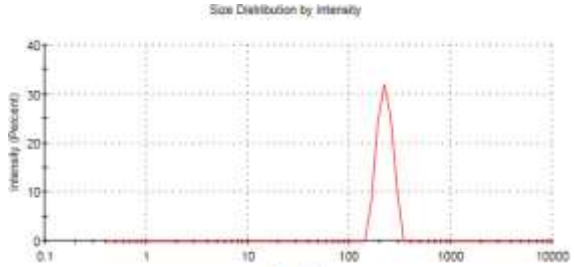
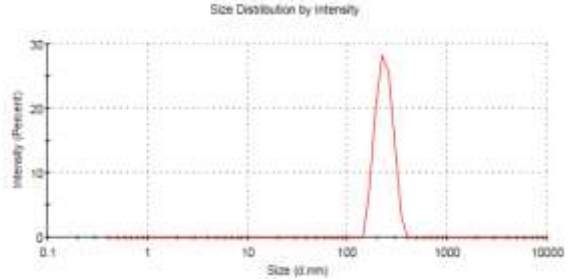


Figure 4. 6: 60% solid content seeded emulsion polymerization

(d)



(e)



(f)

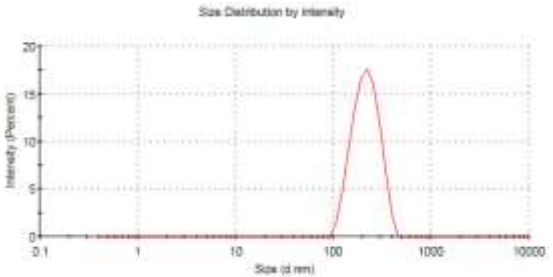
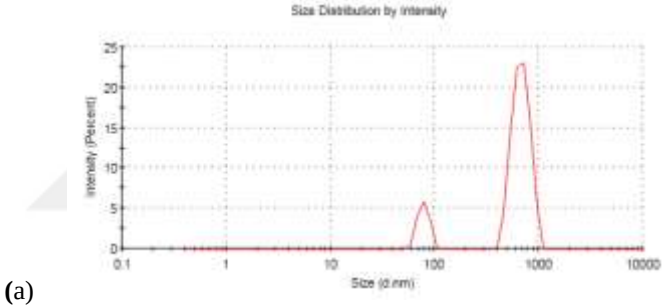
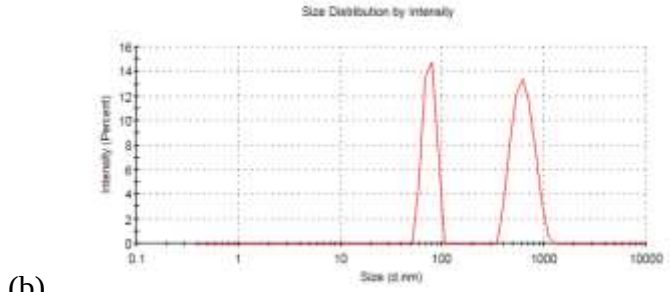


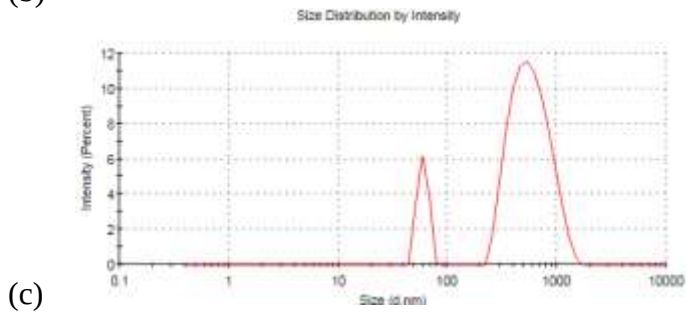
Figure 4. 7 : 65% solid content seeded emulsion polymerization



(a)

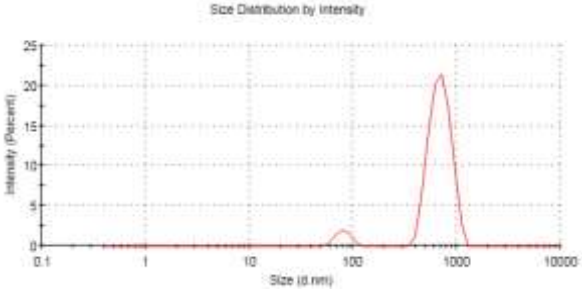


(b)

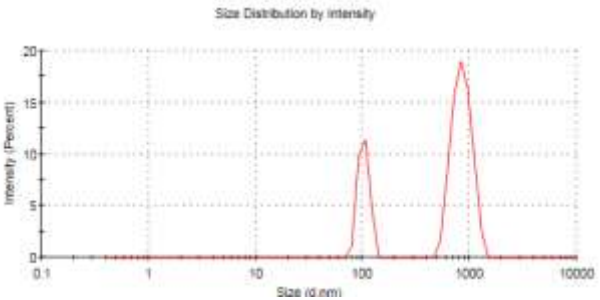


(c)

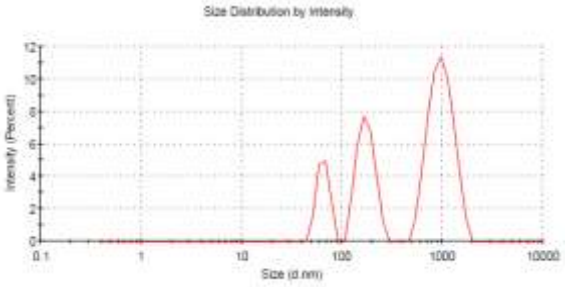
Figure 4. 8 : 60% solid content unseeded emulsion polymerization



(d)



(e)



(f)

Figure 4. 9 : 65% solid content unseeded emulsion polymerization

With the use of a ready-to-use seed or seed latex dispersion, it is possible to determine the number of particles at the beginning of an emulsion polymerization process and thus the final particle size, with a relatively high level of precision. This technique is known as a seed polymerization. It is provides good reproducibility of particle size distribution in every batch. The objective is to use the seed stage to control over particle size and particle size distribution, which will be narrow if the seed stage is short.

In seeded emulsion polymerization, a seed polymer was feeded with pre-emulsion and initiator during the reaction. Monomers were diffused into the micelles and increase in the particle size of seed polymer was observed. In the second hour of feeding, a certain amount of seed was introduced into the reactor shot wise. Due to the addition of the second seed of the polymer particles and thus the increase of the polymerization areas, the conversion at the second polymerization stage was higher than the first [39]. Monomers prefer to diffuse the second seed polymers rather than grown polymers. Therefore, in emulsion polymerization that made in the presence of seed, unimodal particle size distributions are obtained (Fig.4.6- Fig 4.7). Differences in the size of particle were observed that it depends on amount of seed polymers, which added the reaction medium at second hours. It was arise from surfactant amount of added seed.

In unseeded emulsion polymerization, bimodal particle size distributions are obtained. In unseeded emulsion polymerization, reaction medium without seed emulsion was feeded with pre-emulsion and initiator during the reaction. In the second hour of feeding, a certain amount of seed was introduced into the reactor shot wise. Compared to seeded emulsion polymerization, particle size of polymers is large (Fig.4.8-Fig 4.9). If the level of surfactant is too high and / or the concentration of seed particles is too low, new particles may form during monomer addition, leading to broad particle size distribution. [40]. In this situation, Since the particle nucleation is very small in the beginning of reaction, the final particle sizes are very large. Enlargement in the size of particle were obtained that it depends on to increase amount of seed polymers which added the reaction medium at second hours.

It is indicated that particle size of latex of 100 to 200 nm retain their fluidity for solid contents of 50 up to maximum of 55% by weight [10]. Bimodal or multimodal

particle size distribution is necessary for preparing solid contents of more than 60% by weight. The viscosities of latexes consist of the results parallel to the particle size values.

Table 4.5 : Viscosities and surface tension of emulsion copolymers

Predicted Solid Content (%wt)	Seed in the reactor (%wt)	Seed added at 2nd hour (%wt)	Viscosity (mPa*s-1)	Surface Tension (mN/m)
60.00	0.74	3.68	2160	62.95±0.06
60.00	0.74	7.35	1695	63.83±0.32
60.00	0.74	11.00	2130	61.30±0.11
65.00	0.74	3.68	27600	n.d.
65.00	0.74	7.35	27400	n.d.
65.00	0.74	11.00	3390	61.17±0.02
60.00	0.00	3.68	150	53.12±0.14
60.00	0.00	7.35	380	51.69±0.02
60.00	0.00	11.00	246	52.85±0.36
65.00	0.00	3.68	426	55.70±0.15
65.00	0.00	7.35	980	57.77±0.02
65.00	0.00	11.00	784	55.18±0.14

n.d.= no data

In seeded emulsion polymerization, viscosities of 65% solids latexes are significantly higher than the viscosity of 60% solids. When the results are evaluated in their own groups, it is showed that as the width of the particle size distribution increases, the viscosity decreases.

At 60% solid content latexes, viscosities has nearly same. Because, particle size and their distributions are very close to each other.

At 65% solid content latexes, first two latexes has relatively high viscosities, it arise from very narrow particle size distribution. Compared to other, final 65% solid content latex has lower viscosity because of broad particle size distribution.

In unseeded emulsion polymerization, all of the latex has very low viscosity due to the high particle size and bimodality. At 60% solid content latexes, viscosities are quite low and increasing added seed amount viscosities of latexes increase. At 65% solid content latexes, increasing added seed amount viscosities of latexes increase.

However, final latexes viscosities lower than second one due to nucleation. Surface tensions of the latexes were found higher values than unseeded. This condition can explain as described above when adding seed to the reaction medium, introducing amount of polar groups to the polymer chain are higher.

5. CONCLUSION

In this thesis, two different studies were performed. Firstly, new nonionic polyurethane based surfactant was synthesized starting from methoxy PEG-500 and TDI to obtain urethane modified PEG based surfactant (PU).

PU was used in emulsion polymerization of vinyl acetate (VAc) and Methyl methacrylate (MMA)-Butyl acrylate (BA) copolymerization. Obtained latexes remain stable for 3 month.

Emulsion polymerization experiments were investigated depending on time and surfactant quantity. At the same time, these experiments were repeated using anionic surfactant (Dowfax 2A1). Obtained latexes using both different surfactants were characterized by viscosity, surface tension, particle size and molecular weight measurements.

Second part of the thesis, high solid content water-based emulsion polymerization of acrylic monomers experiments were investigated. Therefore, semi-batch reaction system was used in this study. Firstly, poly (MMA-co-BA) seeds were prepared then these seeds were fed to reactor, and then, MMA-BA-MAA monomers were added to prepare high solid content acrylic latexes. In these experiments, anionic surfactant was used.

At the end of reactions, 60%-65% solid content latexes were obtained and particle sizes were determined and bimodal system were obtained successfully.

In addition, some experiments were made without adding seeds at the first stage of polymerization. But, seeds were added to the both system after 2 h.

Besides particle size determinations of the latexes, other characterizations such as viscosity, surface tension and molecular weight measurements were investigated.

There are many parameters could be studied.

In addition, PU/anionic surfactant mixture will be used for semi-batch emulsion polymerization of acrylics.

REFERENCES

[1] Yamak, H. B. (2013). Emulsion Polymerization : Effects of Polymerization Variables on the Properties of Vinyl Acetate Based Emulsion Polymers. *Emulsion Polymerization*, 35–73. https://doi.org/10.5772/51498

[2] de la Cal, J. C., Leiza, J. R., Asua, J. M., & Butte, A. (2005) Emulsion Polymerization. Handbook of Polymer Reaction Engineering. https://doi.org/0.1002/9783527619870.ch6

[3] Harkins W.D (1945) A General Theory of The Reaction Loci in Emulsion Polymerization. J. Chem. Phys. 13:381.

[4] Harkins W.D (1946) A General Theory of Reaction Loci in Emulsion Polymerization. J. Chem. Phys.14:47-48.

[5] Blackley D.C (1975) Emulsion Polymerization, Theory and Practice. London: Applied Science Publishers.

[6] Available: en.wikipedia.org/wiki/Emulsion_polymerization

[7] Gardon J. L (1968) Emulsion Polymerization I. Recalculation and Extension of Smith-Ewart Theory. J. Polym. Sci. A. 6:623-641.

[8] Rudin, A., & Choi, P. (2013). Dispersion And Emulsion Polymerizations. *The Elements of Polymer Science & Engineering*, 427–447. https://doi.org/http://dx.doi.org/10.1016/B978-0-12-382178-2.00010-9

[9] Herk, A. V. (2005). Chapter 3: Emulsion Polymerisation. *Chemistry and Technology of Emulsion Polymerisation*, 47–110.

[10] Schwartz M., Baumstark R. (2001), Free-Radical Polymerization and Emulsion Polymerization, *Waterbased Acrylates for Decorative Coatings*, Hanover, Germany: Vincentz Network.

[11] Farn, R. J. (2007). Chemistry and Technology of Surfactants. Chemistry and Technology of Surfactants. https://doi.org/10.1002/9780470988596

[12] Zhenqian, Z., Bo, X., Pei, W., & Ninyyi, Y. (2015). Hybrid latex particles preparation with seeded semibatch emulsion polymerization. *Colloids and Surfaces A: Physicochemical and Engineering*

Aspects, *482*, 422–430. https://doi.org/10.1016/j.colsurfa.2015.06.050

[13] Elraies, K. A., Tan, I. M., Fathaddin, M. T., & Abo-Jabal, A. (2011). Development of a New Polymeric Surfactant for Chemical Enhanced Oil Recovery. *Petroleum Science and Technology*, *29*(14), 1521–1528. https://doi.org/10.1080/10916460903581427

[14] Schmidt, B. V. K. J., Molinari, V., Esposito, D., Tauer, K., & Antonietti, M. (2017). Lignin-based polymeric surfactants for emulsion polymerization. *Polymer (United Kingdom)*, *112*, 418–426. https://doi.org/10.1016/j.polymer.2017.02.036

[15] Mishra, M., Muthuprasanna, P., Prabha, K. S., Rani, P. S., Babu, I. A. S., Chandiran, I. S., … Shalini, S. (2009). Basics and potential applications of surfactants - A review. *International Journal of PharmTech Research*, *1*(4), 1354–1365.

[16] Abbott, S. (2015). Surfactant Science : Principles and Practice, 1–249. Retrieved from http://www.stevenabbott.co.uk/_downloads/Surfactant Science Principles and Practice.pdf

[17] Salaguer, J.-L. (2002). SURFACTANTS Types and Uses. *Laboratory of Formulation, Interfaces, Rheology and Processes*, *2*, 1–49. https://doi.org/10.1016/j.marpolbul.2013.12.019

[18] Chern C.S (2006) Emulsion Polymerization Mechanisms and Kinetics. Prog. Polym. Sci. 31:443-486.

[19] Michael Y. Pletnev, (2001), *Chemistry of Surfactants*, Surfactants: Chemistry, Interfacial Properties, Applications, Elsevier.

[20] Erbil H.Y (2000) Vinyl Acetate Emulsion Polymerization and Copolymerization with Acrylic Monomers. Florida: CRC Pres.

[21] Lindemann M.K (1967) Vinyl Polymrization. New York: Dekker. Vol 1. Pt 1. 260.

[22] Bovey F.A, Kolthoff I.M, Medalia, A.I, Meehan, E.J (1965) Emulsion Polymerization.High Polymer Series Vol. IX. New York: Interscience Publishers Inc.

[23] Poehlein G., (1986), Emulsion Polymerization, *Encyclopedia of Polymer Science and Engineering*, Wiley, New York.

[24] Rudin, Alfred, (2013), The Elements of Polymer Science & Engineering, *Chapter 10 Dispersion and Emulsion Polymerizations*, Elsevier.

[25] Arthur A. Tracton, (2007) Coating Materials and Surface Coatings

[26] Gilbert R. (1995). Emulsion Polymerization, A Mechanistic Approach, *Academic Press*, San Diego, CA.

[27] Sørensen, Per Aggerholm, "Anticorrosive coatings: a review." *Journal of Coatings Technology and Research* 6.2 (2009): 135-176.

[28] Poth U., Schwalm R. and Schwartz M. (2011), Emulsion Polymerization, *Acrylic Resins*:, *45*, Hanover, Germany: Vincentz Network.

[29] Mariz, I. de F. A., de la Cal, J. C., & Leiza, J. R. (2010). Control of particle size distribution for the synthesis of small particle size high solids content latexes. Polymer, 51(18), 4044–4052. https://doi.org/10.1016/j.polymer.2010.07.001

[30] Mariz, I. de F. A., Leiza, J. R., & De la Cal, J. C. (2011). Competitive particle growth: A tool to control the particle size distribution for the synthesis of high solids content low viscosity latexes. Chemical Engineering Journal, 168(2), 938–946. https://doi.org/10.1016/j.cej.2011.02.023

[31] Guyot, A., Chu, F., Schneider, M., Graillat, C., & McKenna, T. F. (2002). High solid content latexes. Prog. Polymer Sci., 27, 1573–1615.

[32] Ai, Z., Deng, R., Zhou, Q., Liao, S., & Zhang, H. (2010). High solid content latex: Preparation methods and application. Advances in Colloid and Interface Science, 159(1), 45–59. https://doi.org/10.1016/j.cis.2010.05.003

[33] Chu F, Guillot J, Guyot A. Polym Adv Technol 1998;9:844.

[34] Schneider M, Graillat C, Guyot A, McKenna TF. J Appl Polym Sci 2002;10:1916

[35] Eliseeva V.I, Ivanchev S.S, Kuchanov S.I, Lebedev A.V (1981). Emulsion Polymerization and Its Applications in Industry. New York: Plenum Publishing Corporation.

[36] Wicks Z., Jones F., Pappas S. (2007), Acrylic Resins, *Organic Coatings*, Third Edition, John Wiley & Sons.

[37] R. Hoffman, Factors affecting the viscosity of unimodal and multimodal colloidal dispersion, J. Rheol. 36,5 (1992) 947-965

[38] Yang, M., & Dan, Y. (2003). Preparation and characterization of the complex latex formed through complexation of two polymer latexes with chemically complementary structure. *Journal of Applied Polymer Science*, *89*(5). https://doi.org/10.1002/app.11992

[39] Chu, F., Guillot, J., & Guyot, A. (1998). Study of Poly (St / BA / MAA) Copolymer Latexes with Bimodal Particle Size Distribution, *857*, 851–857.

[**40] Lovell, P. A. (1997). Lovell, Peter A**. - 1997 - Emulsion Polymerization and Emulsion Polymers. *Emulsion Polymerization and Emulsion Polymers*.

[41] R. G. Gilbert. Emulsion polymerization: A mechanistic approach. Academic Press, San Diego, 1995.

[42] C. D. Immanuel, C. F. Cordeiro, S. Sundaram, E. S. Meadows, T. J. Crowley, and F. J. Doyle. Modeling of particle size distribution in emulsion co-polymerization: Comparison with experimental data and parametric sensitivity studies. Comp. Chem. Engng., 26(7-8):1133–1152, 2000

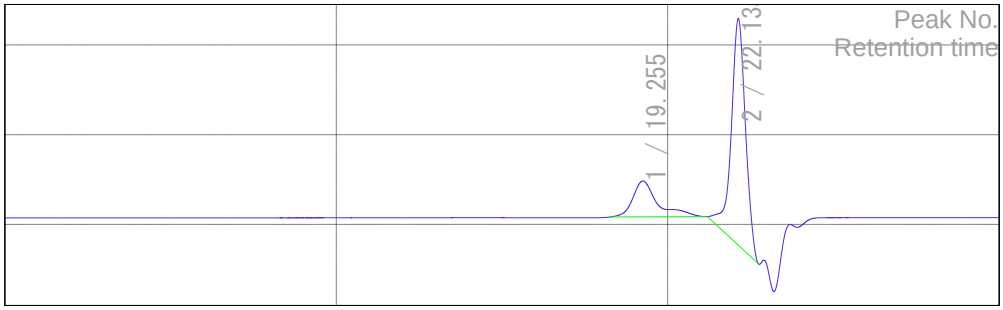
APPENDICES

APPENDIX A

Chromatogram report

Header

Title		Data acquisition date and time	2017/10/17 10:20:34
Sample name	178-İtü TDI-PEG500	Calculation date and time	2018/03/07 14:50:33
Database name	2017-10-17.chd	Acquisition time [min]	0.000 - 30.000
Data name	RSLT0001	Sampling interval [msec]	100
Method name	BETEK-Conventional-METOD-PMMA	Cup number	1
Channel	RI	Calculation type	Molecular Weight



Result of molecular weight calculation (RI)

Peak 1 Base Peak

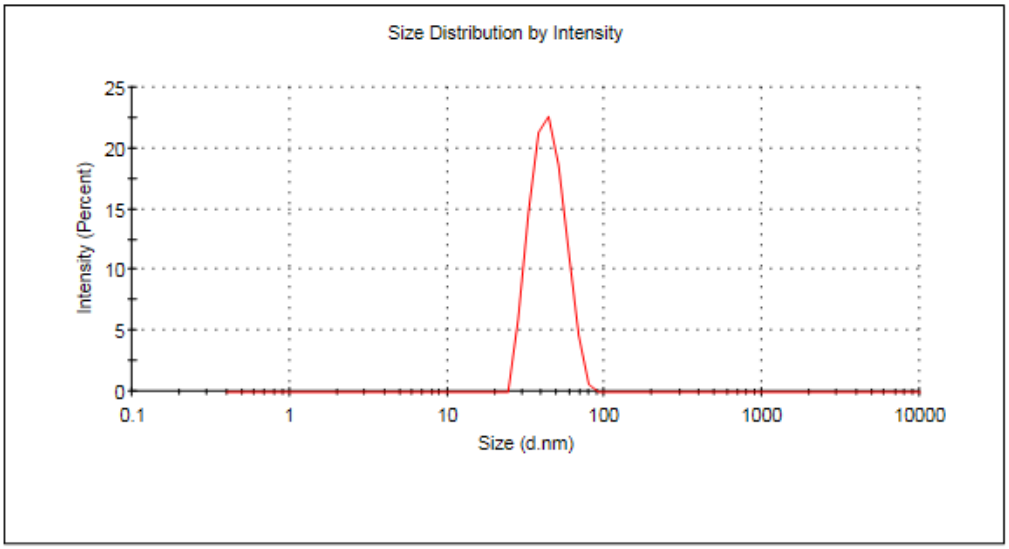
	[min]	[mV]	[mol]		
Peak start	18.265	8.319	3,202	Mn	1,159
Peak top	19.255	48.532	1,477	Mw	1,354
Peak end	21.135	8.670	306	Mz	1,509
				Mz+1	1,636
				Mv	1,354
Height [mV]			40.092	Mp	1,489
Area [mV*sec]			2083.352	Mz/Mw	1.115
Height% [%]			13.678	Mw/Mn	1.168
[eta]			1353.70831	Mz+1/Mw	1.209

APPENDIX B

Size distribution of seed

Results

			Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	42,71	Peak 1:	44,33	100,0	10,49
PdI:	0,108	Peak 2:	0,000	0,0	0,000
Intercept:	0,964	Peak 3:	0,000	0,0	0,000
Result quality	Good				



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