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Catalytic emulsion polymerization of norbornene

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CATALYTIC EMULSION POLYMERIZATION OF NORBORNENE

BY

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B.S. Chemical Engineering, University of New Hampshire, 2005

THESIS

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This thesis has been examined and approved.

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May 11, 2007

Date

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ABSTRACT

CATALYTIC EMULSION POLYMERIZATION OF NORBORNENE

by

Diane E. Crosbie

University of New Hampshire, May, 2007

The use of late transition metal catalysts for the polymerization of olefins in aqueous media has created new opportunities to produce latex particles based on ethylene and its olefinic derivatives. This thesis reports on three different aspects of the catalytic emulsion polymerization of norbornene; 1) reaction parameters (e.g. reaction temperature, ionic strength), 2) addition of various classes of surfactants, and 3) polymerization of a variety of norbornene-derived monomers. These reactions have been carried out as *ab initio* batch emulsion polymerizations using allyl palladium catalysts and a lithium based activator, supported by a variety of surfactants.

The role of surfactants in traditional emulsion polymerization is to assist in particle nucleation and/or to stabilize latex particles. We studied the role of several classes of surfactants in the emulsion polymerization of norbornene with Pd catalysts, both with and without the activator LiFABA. In the catalytic emulsion polymerization of norbornene, some of these surfactants were found to act as weakly coordinating anions with the Pd based catalysts to promote polymerization. When the base latex recipe

already contains an activator specifically designed to work effectively with Pd in organic media (e.g. LiFABA), certain classes of surfactants (e.g. sulfates) act to provide an alternative pathway for polymerization and latex particle formation. Other surfactants (e.g. cationics) can actually suppress all or part of the polymerization by destructively interfering with either the catalyst or the activator. Alkyl sulfates and sulfonates were both effective activators of allyl Pd catalysts and produced latex particles (ca. 40–50 nm) without significant amounts of coagulum. This activity is significantly dependent on the alkyl chain length, and alkyl sulfate anions are more active than the equivalent alkyl sulfonate anions. Cationic, fatty acid and non-ionic surfactants produced variable, but ineffective, results in our studies.

This work determined that the n-alkyl norbornenes can be polymerized in aqueous emulsion and that the mechanisms for latex particle formation are the same as that for norbornene monomer alone. As in the case of norbornene, large amounts of coagulum can be formed if the catalyst and activator are allowed to reach the emulsified monomer droplets and effect polymerization in that location. As the substituents on the norbornene become larger and non-polar, it is necessary to consider their effect on the water solubility of the monomers in order to analyze the experimental results in an effective manner. Our studies included butyl and decyl-norbornene, vinyl and butenyl-norbornene, and methanol-norbornene in *ab initio* emulsion polymerization and also the mini-emulsion polymerization of decyl-norbornene.

CHAPTER 1

INTRODUCTION

Organization of this Thesis

This thesis is divided into five chapters, each describing a different aspect of the work on catalytic emulsion polymerization of norbornene and associated monomers. The first chapter provides background information about catalytic and free radical polymerization as well as the motivation of this work. Basic aspects of norbornene polymerization in solution and emulsion are explained, including polymerization and particle formation mechanisms. The second chapter describes in detail the experimental and analytical methods for latex preparation and characterization.

The next three chapters are the crux of the thesis work. Each chapter examines the emulsion polymerization of olefins, but various parameters are altered in each chapter to examine their effect on catalytic activity and latex characteristics. Chapter 3 covers the emulsion and solution polymerization of norbornene using two similar catalysts. Catalyst, activator, and surfactant concentrations, ionic strength, and reaction temperature were varied. The goal of Chapter 3 is to report on the catalytic emulsion polymerization of norbornene and to describe its sensitivity (or insensitivity) to various changes in reaction conditions. Chapters 4 and 5 concern studies on the effect of a variety of surfactants on the catalytic emulsion polymerization of norbornene, and on a variety of norbornene-derived monomers, respectively. The content of chapters 3, 4, and 5 have individually been submitted for publication in *Macromolecules*[1-3]. Each chapter presents its own abstract and conclusions sections. An overall set of conclusions, encompassing all of the chapters, is offered in Chapter 6.

Background on Emulsion Polymerization

Emulsion polymerization is an economically important and common industrial process. It is used to produce synthetic latex that is comprised of polymer particles, typically 50–500 nm in diameter, dispersed in an aqueous phase. The latex can be produced at atmospheric pressure and temperatures from 40 to 95°C, making production relatively safe in a standard stirred tank reactor. Billions of pounds of latex are produced worldwide every year. Their applications range from paints and adhesives, to impact modifiers for engineering thermo-plastics, and to synthetic rubber. Environmentally, emulsion polymerization is extremely safe because water is the continuous medium. This is particularly important because more stringent environmental regulations require that the volatile organic compound levels are as low as possible. Water also provides easy handling and good heat transfer in the reactor. Emulsion polymerization allows high molecular weight polymers to be produced without an increase in latex viscosity, making processability vastly easier than bulk polymerization.

The majority of latex paints are made using acrylic monomers and are relatively expensive. Less expensive monomers, such as olefins, are being examined for paint applications. Unlike acrylates, olefins cannot be polymerized using standard free radical polymerization routes. Rather, olefins are polymerized using transition metal catalysts. Polymerizing olefins using catalysts allow for well defined polymer architecture, inherent UV resistance, and a new range of mechanical properties[4-13].

The olefins of interest for catalytic polymerization are the α-olefins, such as ethylene, and strained-cyclic olefins, such as norbornene. Polyethylene has a low glass transition temperature, T_g, of -120°C whereas polynorbornene has an extraordinarily high T_g ~300°C[13]. Copolymerizing these two monomers would allow the production of a large range of T_g's as well as highly durable and chemically resistance polymers. The ethylene homopolymer is crystalline and thus will not film-form when cast from a water-based latex. Copolymerization is likely to break the crystallinity of polyethylene and allow easy tailoring of the T_g for film forming polymers. Additionally there is a family of norbornenes, such as acetyl, butyl, decyl, etc., in which the substituents decrease the T_g of the polymer. This offers many opportunities to make latices with interesting and useful properties.

The mechanism of particle nucleation in free radical emulsion polymerization is well known to occur via micellar or homogeneous nucleation[14-16]. A schematic of this particle nucleation can be found in Figure 1. The oligomers are formed in the water phase and either enter a micelle or precipitate. Once particles are formed, there are three places for polymerization to occur; water phase, particle surface, and inside the particle. Particle size is controllable by the temperature, the amounts of surfactant and initiator, and the amount of monomer added to the reactor. Once particles are formed, the resulting monomer will polymerize within those particles, barring the existence of micelles. The molecular weight increases through propagation and is stopped through chain transfer and termination reactions. In contrast, catalytic emulsion polymerization produces active polymer chains that cannot terminate with another polymer chain like free radical emulsion polymerization can, but rather the growing chains can be stopped through chain transfer reactions or deactivation of the catalyst. These contrasting mechanisms may result in differences in the mechanisms of particle nucleation and growth, and molecular weight development between catalytic and free radical emulsion polymerization. A review of norbornene polymerization is presented below.

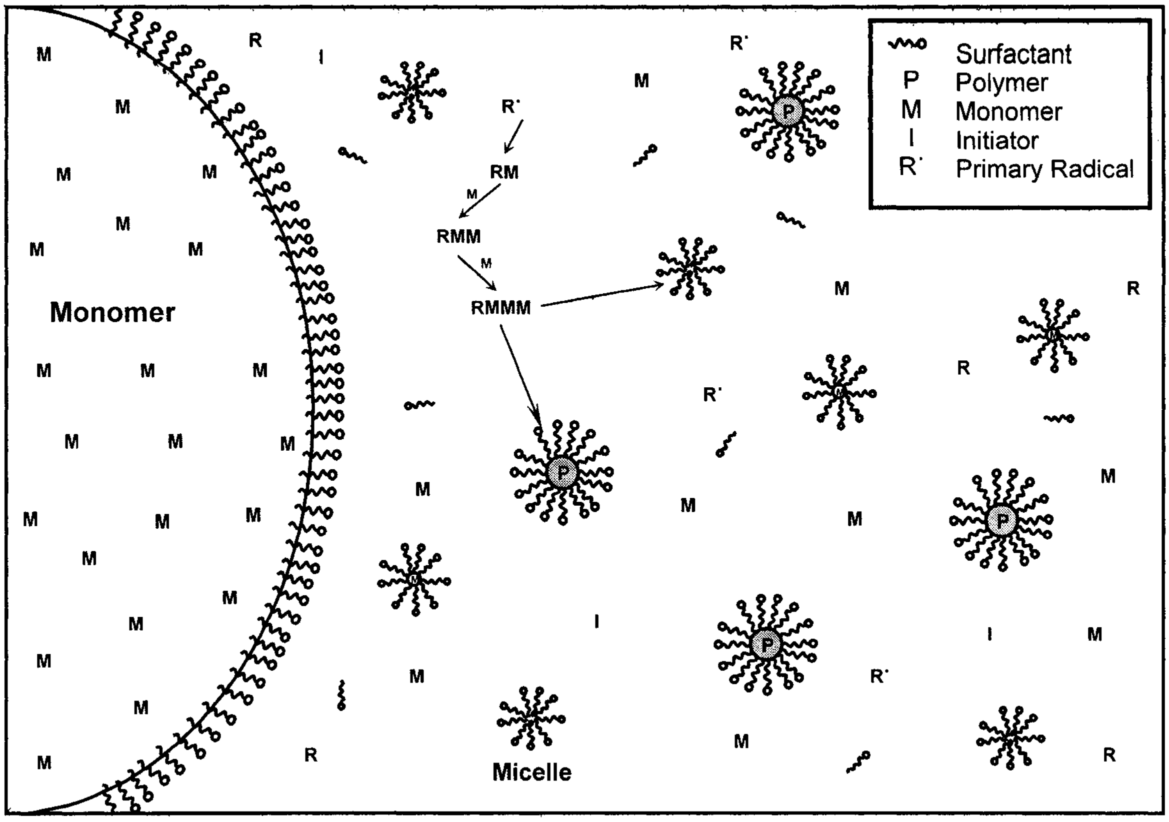


Figure 1. Schematic of particle nucleation via free radical emulsion polymerization.

Background on Norbornene Polymerization

Norbornene, or bicyclo[2.2.1]hept-2-ene, can be polymerized via three different routes shown in Figure 2. The most common polymerization of norbornene is ring-opening metathesis polymerization (ROMP)[17]. The polymerization route opens the strained ring and leaves the double bond intact. This polymer is produced industrially and sold under the trade name Norsorex®. The polymerization occurs in air using a $RuCl_3/HCl$ catalyst in butanol. The glass transition temperature (T_g) of ROMP polynorbornene is 37°C. The residual double bonds can be crosslinked to produce an elastomeric material that is used for oil spill recovery and in vibration and sound damping materials[18].

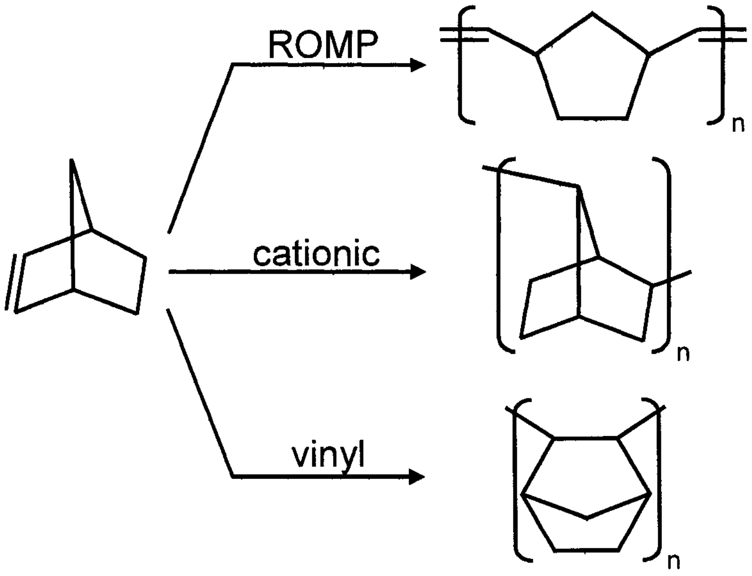


Figure 2. Three different routes to polymerize norbornene

Relatively little is known about cationic polymerization of norbornene. Recently, Myagmarsuren et al.[19] achieved high molecular weight (M_W = 76,300-307,400 g/mole) polynorbornene via cationic polymerization with a T_g range from 346–365°C. They used $Pd(Acac)_2/BF_3OEt_2$ as the catalyst system in a toluene solution.

Vinyl polymerization of norbornene leaves the bicyclic structure intact and polymerizes through the double bond. This polymer has gained attention in recent years for its many interesting applications and properties. Polynorbornene has a high T_g (>300°C), optical transparency, low birefringence, and low moisture absorption[20]. Norbornene is readily synthesized by the Diels-Alder reaction of cyclopentadiene and a dienophile. The dienophile can contain a variety of functional groups, adding functionality to the polymer and changing its properties (e.g. adding a long alkyl chain will decrease the polymer T_g). A Diels-Alder reaction to make a norbornene-derived monomer can be found in Figure 3.

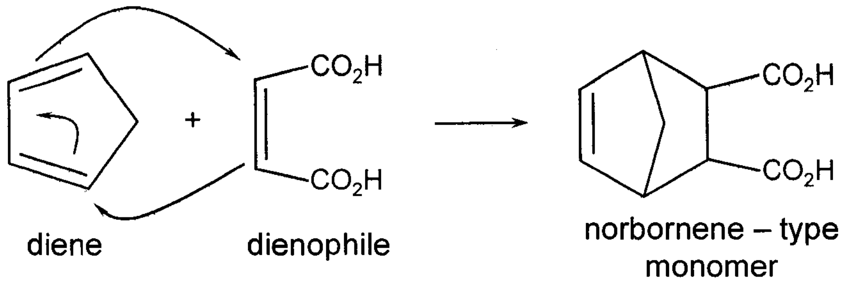


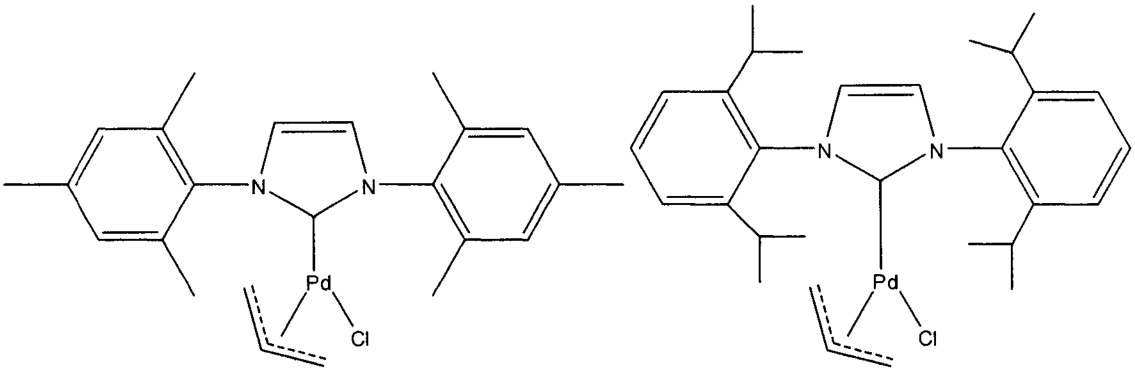
Figure 3. Preparation of cis-norbornene-5,6-endo-dicarboxylic anhydride via a Diels-Alder reaction[21].

Copolymerization of ethylene and norbornene in organic solution is produced by Ticona and Mitsui Chemicals under the trade name TOPAS (Thermoplastic Olefin Polymers of Amorphous Structures). The T_g of polyethylene is -120°C, although it is not soft at room temperature because it is crystalline. The addition of polynorbornene breaks the crystallinity as well as increases the T_g by introducing the rigid cyclic structure. The norbornene-ethylene copolymer has been prepared using a zirconium, titanium, or palladium based catalyst[22-25]. This line of copolymers has excellent transparency, high stability against hydrolysis and chemical degradation, and processability. TOPAS™ polymers are used in heat resistant applications and compact discs. Many researchers have begun studying the stereochemistry and effect of various amounts of each monomer on the mechanical properties of these TOPAS polymers[22-25].

Solution Polymerization of Norbornene

It has been shown that norbornene can be polymerized in solution with Ni and Pd based catalysts through vinyl polymerization in the temperature range of 25–75°C[26-38]. The molecular weights reported were between 400 and 300,000 g/mole. Monomer conversions ranged from as low as 20% to as high as 100%. Some researchers[20,26-34,39-41] found that polynorbornene was soluble in standard solvents such as tetrachloroethene, xylene, cyclohexane, and chloroform, while others[34-38,42,43] found that polynorbornene was insoluble in those same solvents. This may be due to crystallization of polynorbornene at higher molecular weights[36]. The most common catalyst for vinyl polymerization of norbornene is $PdCl_2$. This basic catalyst yields low molecular weight polymers. The addition of large ligands on to the palladium center can increase monomer addition selectivity[44].

A recent patent submitted by Rohm and Haas[33] shows the robust activity of two catalysts that homopolymerize and copolymerize norbornene, norbornene derivatives, and acrylates in solution. The catalysts used were allyl palladium chloride 1,3(bis(2,4,6-trimethylphenyl)imidazole-2-ylidene) (TMP) and allyl palladium chloride 1,3(bis(2,6-diisopropylphenyl)imidazole-2-ylidene) (DPP) whose structures are found in Figure 4. These catalysts were activated by a variety of weakly coordinating anion activators, most notably $AgPF_6$, $AgSbF_6$, and LiFABA (the latter structure is found in Figure 5).



(a) (b)

Figure 4. Structure of catalysts. (a) TMP, (b) DPP

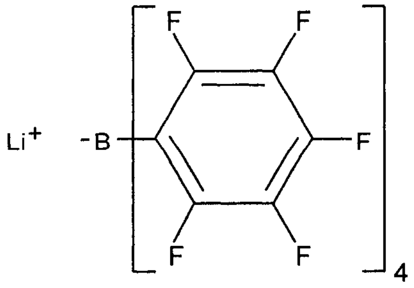


Figure 5. Structure of the activator, LiFABA

As shown in Figure 6, the weakly coordinating anion pulls the chlorine off of the catalyst in organic media, leaving a vacancy. The monomer, in this case norbornene, coordinates with the palladium. The insertion step may occur through the allyl group via the Cossee mechanism, which is detailed elsewhere[17].

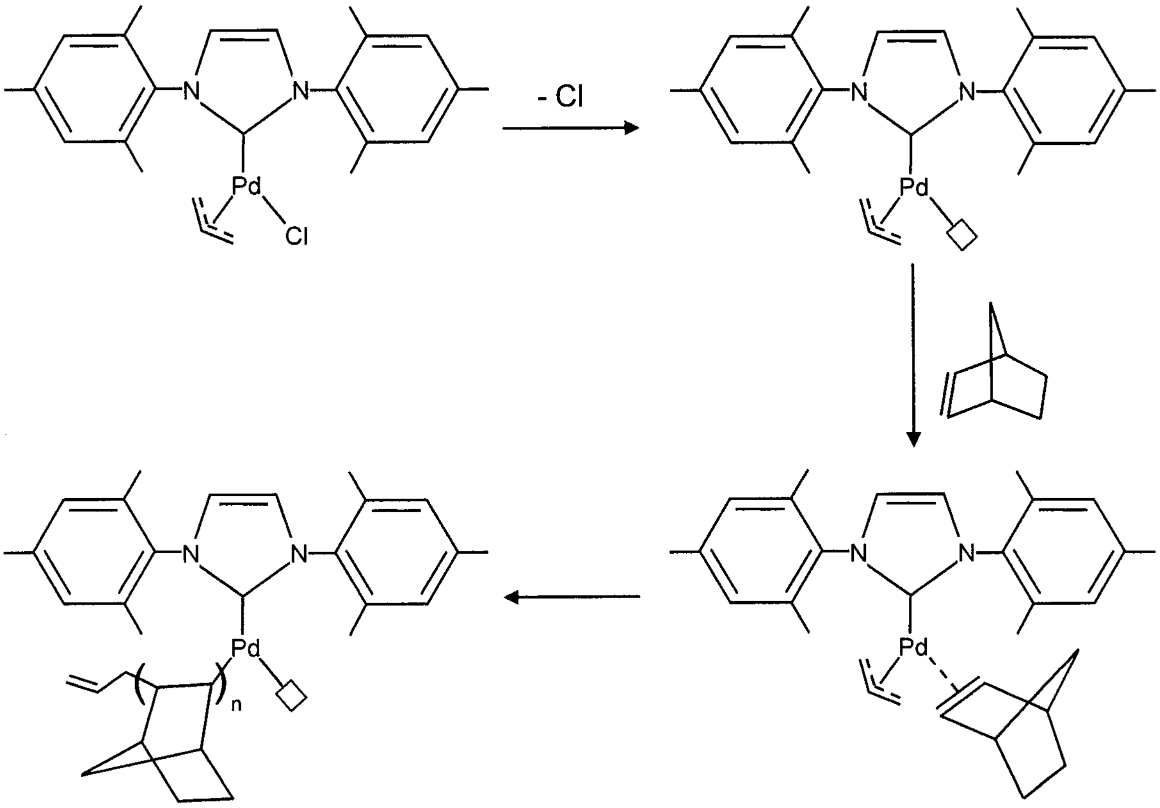


Figure 6. Potential mechanism of polymerization for norbornene with TMP catalyst.

Emulsion polymerization is the preferred method of polymerization for environmental reasons. Polymerizing norbornene and norbornene copolymers in an aqueous environment would be more environmentally beneficial and also increase the ease of manufacturing processability.

Emulsion Polymerization of Norbornene

Norbornene has been polymerized in aqueous emulsion environments before. Eychenne et al.[43] and Novak et al.[41] published in 1993 about the aqueous polymerization of norbornene and diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, respectively. They both used $PdCl_2$ as their catalyst. Eychenne used sodium dodecyl sulfate (SDS) as the surfactant and produced small particles with a diameter of 10–20 nm. They found that the polymer molecular weight increased as their SDS concentration increased. Oligomeric polynorbornene was formed even with high polymer yields which they proposed was due to the sulfate head group of the SDS complexing with the palladium and leading to chain terminations without catalyst deactivation. Eychenne also investigated a polymerization without surfactant. Unlike the emulsion polymer made with surfactants, the polymer without surfactant precipitated out of the solution and was insoluble in solvents they tried.

Lipian et al.[31] found that some palladium complexes efficiently polymerized the functionalized norbornene, butyl-norbornene, in water. They used $[(\eta^3\text{-allyl})Pd(Cl)]_2$ catalyst precursor, $P(m\text{-}C_6H_4SO_3Na)_3$ ligand, and LiFABA activator with SDS for the emulsion polymerization and obtained 89% conversion at 65°C over a period of 4 hours. A bimodal particle size distribution was obtained with large 'beads' around 5 μm and 30–50 μm in diameter. A polymer molecular weight around 1 million g/mole was achieved with a polydispersity index of 2.7. Lipian showed that these palladium catalysts could retain high activity in water. They claim that high catalyst activity was obtained with coordination of the phosphine ligand to a cationic palladium center in the presence of the weakly coordinating FABA anion.

Chemtob et al.[42] recently reported the polymerization of norbornene using mini-emulsion techniques. A typical mini-emulsion involves the sonication of monomer in water with surfactant to form droplets in the 100–500 nm range. The polymerization occurs in the monomer droplets and thus results in polymer particles that are the size of the monomer droplets. Chemtob used two palladium based catalysts; water soluble and water insoluble. These two catalysts are the same as the catalysts that Lipian used in aqueous environments. When Chemtob did not sonicate to create the mini-emulsion, they found large amounts of coagulum (>20%) as well as polymer particles that were greater than 1 μm. The polymer was not soluble in any solvents that were tried, therefore the molecular weight was not determined. They proposed that they made a high molecular weight polymer because of its insolubility as well as its high thermal stability. Interestingly, they were not able to observe a T_g even when heating to 500°C in a differential scanning calorimeter. They also examined various surfactants and found that sodium dodecyl sulfate (SDS) yielded the most stable polymer particles 80–200 nm in diameter.

Objectives of this Thesis

This thesis describes studies of the polymerization of norbornene in an aqueous emulsion environment with a transition metal catalyst and a weakly coordinating anion activator. In particular, the effect of catalyst, activator, and surfactant concentrations, ionic strength, reaction temperature, and surfactant and monomer types on the overall catalytic activity of norbornene emulsion polymerization was investigated.

Previous work has investigated the catalytic polymerization of olefins in organic solutions[4-13,26-38]. In organic solutions, additives such as surfactants are not required because polymer particles are not being created. Surfactants are required in latices as a stabilizer to prevent coagulation of particles. Many of these surfactants are ionic and have the potential for coordinating with the catalyst or activator in catalytic emulsion polymerization, as both of these species are also charged. This work investigates the interaction of these charged surfactant molecules with the catalyst and activator.

The addition of substituents on the norbornene monomer could decrease the polymer T_g, increase adhesion to substrates, or allow the polymer to be functionalized through secondary reactions. Various norbornene based monomers may also interact negatively with the catalyst by the substituent coordinating with the active site. If the monomer can coordinate with the catalyst, the polymerization may be hindered or completely shut down. Various norbornene-derived monomers are investigated to see if the polymerization is hindered by the addition of certain substituents.

This work represents the first study that has systematically investigated the effects of catalyst, surfactant type and level, and norbornene monomer type on emulsion polymerization of norbornenes. The goal is to elucidate the reaction mechanism of catalytic emulsion polymerization of norbornene, extended more generally to olefins, as well as to determine the effect of various additives on the production of norbornene latices.

CHAPTER 2

EXPERIMENTAL AND ANALYTICAL METHODS

Chemicals

Norbornene (99%, Aldrich), 5-butyl-2-norbornene (Rohm & Haas), 5-decyl-2-norbornene (Promerus), 5-vinyl-2-norbornene (95%, Sigma Aldrich), 5-butenyl-2-norbornene, and 5-methanol-2-norbornene (95% City Chemical) were used as received. Allylchloro[1,3-bis(2,6-di-i-propylphenyl)imidazol-2-ylidene] palladium (97%, Strem Chemical) (henceforth referred to as DPP) and Allylchloro[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] palladium (Rohm & Haas) (henceforth referred to as TMP) were the catalysts and also used as received. The structures of catalysts are shown in Figure 4. Lithium tetrakis(pentafluorophenyl) borate (LiFABA) (Boulder Scientific) was the activator and used as received. The structure of this activator is shown in Figure 5. The catalysts and activators are oxygen sensitive and were kept in an MBraun glove box to ensure stability. Sodium decyl sulfate (Acros) (SDecS), sodium dodecyl sulfate (99%, Alfa Aesar) (SDS), sodium tetradecyl sulfate (95%, Acros) (STDS), sodium hexadecyl sulfate (99% Alfa Aesar) (SHDS), and sodium octadecyl sulfate (93%, Aldrich) (SODS) were used as received. Rhodapex CO-436 (Rhodia), sodium stearate (99%, Sigma), tetrasodium pyrophosphate (TSPP) (≥95%, Sigma), dodecyl benzene sulfonic acid (Acros) (DBSA), sodium 1-hexadecane sulfonate (98%, Avocado Research Chemicals), Aerosol OT (EM Chemicals), and cetyl-trimethylammonium bromide (CTAB) were used as received. Igepal CO-520 and CO-997 (Rhône Poulenc) and Igepal CO-720 and CO-890 (Aldrich) were used as received.

Deionized water from a Corning Mega Pure^{TM} D2 water purification system was used in all experiments. Acetone (99.5%, EMD Chemicals) and tetrahydrofuran (99.9%, EMD Chemicals), and cyclohexane (99.9%, Fisher Scientific) were used as received.

Procedure and Experimental Conditions

Latex Preparation

Distilled water was boiled and purged with argon for 30 minutes to eliminate the oxygen. Norbornene was dissolved in acetone in a ratio of 9:1 to ease the transfer of norbornene to the reactor because it is solid at room temperature (T_m = 45°C). The other norbornene-derived monomers are liquid at room temperature, thus the acetone was omitted in those experiments. Surfactant was also dissolved in water to ease the transfer into the reactor. The SDS concentration was designed to be well below the critical micelle concentration (cmc). The other sodium alkyl sulfate surfactants were designed to have the same molar concentration as SDS (9×10^{-3} M in water), and thus could be above their cmc (i.e., sodium tetradecyl sulfate, cmc = 2.1×10^{-2} M at 25°C[42]). Both solutions (monomer and surfactant) were purged with argon for 10 minutes. The reaction was carried out in a 125mL, three-neck, water-jacketed glass reactor equipped with a magnetic stirring bar. The stirring was adjusted to have enough of a vortex that monomer pooling was not observed in the reactor. The reaction temperature was controlled by means of a water bath and the reactor was evacuated and purged with argon. The above solutions were cannulated into the reactor using argon pressure and then the reactor was brought up to temperature, typically 60°C. The catalyst and activator were dissolved separately in 0.5 g THF, to produce solutions of 0.013 M and 0.016 M, respectively, and then transferred out of the glove box. The catalyst solution was injected into the reactor followed by the activator solution. After the reaction was complete, the polymer latex was filtered through eight layers of cheese cloth to separate coagulum present in the latex. A standard polynorbornene recipe is shown in Table 1. Solution polymerizations were also carried out by following the same procedure as above but removing the SDS and replacing the water with cyclohexane.

Table 1. Standard polynorbornene polymerization recipes

Polymerization Recipes

	Emulsion	Solution
DI Water	95 g	----
Cylcohexane	----	95 g
Monomer	5 g	5 g
Acetone	0.5 g	0.5 g
SDS	0.25 g	----
Catalyst	3.2 mg	3.2 mg
Activator	5.6 mg	5.6 mg
THF	1 g	1 g
Temperature	60 °C	60 °C

Latex Characterization

Latex Conversion

Latex conversion was measured gravimetrically after evaporating the volatile compounds in a conventional oven at 60°C. The total coagulum level was determined from the amount of polymer left in the reactor after removal of the latex (i.e. wall scale) and that separated by filtration through cheesecloth. The overall conversion was calculated as the sum of the latex conversion and the coagulum conversion. The solids content is the mass of the polymer solids/ total mass of latex. Two samples were taken from the latex and dried in an aluminum pan. The solids content values are the average of the two samples, and the measurements usually agree within a few tenths of one percent. Reaction rates were observed by sampling the latex as a function of time.

Particle Size

Particle size distributions of the final latices were measured by light scattering (Microtrac Nanotrac^{TM} 250) and capillary hydrodynamic fractionation (Matec CHDF2000) as well as compared to Scanning Electron Microscopy (Amray 3300FE) (SEM) images. The latex was diluted in deionized water, with a solid content <0.01%. A droplet of the dilution was dried on a pure polished carbon wafer that was mounted on a SEM specimen stub with low resistant contact cement. The dried samples were sputter-coated with ~50Å of platinum and observed in the SEM.

Molecular Weight Determinations

The molecular weight distributions of the solution polymerization of norbornene, 5-butyl-2-norbornene, and 5-decyl-2-norbornene were determined by gel permeation chromatography (GPC). The GPC system consisted of Waters components and a refractive index and ultraviolet detector. There were four Styragel columns connected in series; three HMW6E and one HMW7 column. The columns were calibrated using polystyrene standards from Polysciences Inc. Polymers were formed in cyclohexane solution and diluted in chloroform to a concentration of 0.5 wt% polymer. The polymer solution was filtered through a 0.45 μm syringe filter before injection into the GPC.

CHAPTER 3

AB INITIO POLYMERIZATION OF NORBORNENE

Abstract

It has recently been shown that it is possible to polymerize homo- and copolymers of olefins in aqueous media by using late transition metal catalysts. This has opened a new set of opportunities to produce simple and composite latex particles based on ethylene and its olefinic derivatives. Here we report some of our experience in creating water based latices from the strained cyclic olefin, norbornene. This has been done as *ab initio* batch emulsion polymerizations using two different allyl palladium catalysts and a lithium based activator as substitutes for the free radical initiator in standard emulsion polymerization. Such experiments produce small latex particles (ca. 50 nm) and can be burdened with large amounts of coagulum. In studying the effects of catalyst levels, ionic strength, and temperature on the reaction rates, conversion levels, and particle size, we have determined that the coagulum is produced by the migration of the catalyst and activator to the emulsified monomer droplets, producing large agglomerates of ~10 μm polymer particles. After separating out the coagulum, the latices are stable for over a year. It has also become clear that in the aqueous environment, the lithium activator is not necessary to promote emulsion polymerization, and that without it we eliminate the coagulum. Apparently, the surfactant (in our case SDS) works as a weakly coordinating anion with the Pd catalyst. This work has shown that Pd catalysts can tolerate direct injection into the water and that it is not necessary to use mini-emulsion polymerization techniques to produce stable polynorbornene latices.

Introduction and Background

During the past decade, it has been demonstrated[4-13] that late transition metal catalysts are capable of producing some aqueous based latices of polyolefins and their copolymers with a few vinyl monomers. The use of such latices as aqueous based coatings with low VOC offers numerous possible advantages over free radically derived latices including low cost monomers, well defined polymer architecture, new ranges of mechanical properties, inherent UV resistance, etc. This opportunity has led us to begin a research program based upon the catalytic emulsion polymerization (Cat EP) of polyolefins with the objective of elucidating the independent and combined mechanisms of polymerization reactions and polymer particle nucleation and growth. In those efforts, we have tried to compare and contrast our findings and ideas to those inherent to traditional free radical emulsion polymerizations (FR EP).

The olefins of interest are α-olefins, such as ethylene, and strained-cyclic olefins, such as norbornene. Polyethylene has a low glass transition temperature (T_g) of -120°C whereas polynorbornene has an extraordinarily high T_g ~300°C[13]. Copolymerizing these two monomers would allow the production of a large range of T_g's as well as obtaining highly durable and chemically resistance polymers. The ethylene homopolymer is crystalline and thus will not film-form when cast from a water based latex. Copolymerization is likely to break the crystallinity of polyethylene and allow easy tailoring of the T_g for film forming polymers. Additionally there is a family of norbornenes, such as acetyl, butyl, decyl, etc., in which the substituents decrease the T_g of the polymer. This offers many opportunities to make latices with interesting and useful properties.

The mechanism of particle nucleation in FR EP is well known to occur via micellar or homogeneous nucleation. The oligomers are formed in the water phase and either enter a micelle or precipitate. Once particles are formed, there are three places for polymerization to occur; water phase, particle surface, and inside the particle. Particle size is controllable by the temperature, the amounts of surfactant and initiator, and the amount of monomer added to the reactor. Once particles are formed, the resulting monomer will polymerize within those particles, barring the existence of micelles. The molecular weight increases through propagation and is stopped through chain transfer and termination reactions. In contrast, Cat EP produces active polymer chains that cannot terminate with another polymer chain like FR EP can, but rather the growing chains can be stopped through chain transfer reactions or deactivation of the catalyst. These contrasting mechanisms may result in differences in the mechanisms of particle nucleation and growth, and molecular weight development between Cat and FR EP.

It has been shown that norbornene can be polymerized in <u>solution</u> with Ni and Pd based catalysts through vinyl polymerization in the temperature range of 25–75°C[19,20,28,32,34]. The molecular weights reported were between 400 and 300,000 g/mole. Monomer conversions ranged from as low as 20% to as high as 100%. Only a few authors have polymerized norbornene or substituted norbornene monomers in aqueous based emulsions. Puech et al.[39] were the first to report the aqueous polymerization of norbornene via vinyl polymerization. Their catalyst was $PdCl_2$ and produced low molecular weight oligomeric polynorbornene. They found that an increase in their surfactant (SDS) level increased the molecular weight of the polymer and that the latex particles formed were only 10–20 nm in diameter. Lipian et al.[31] reported the polymerization of butyl-norbornene in aqueous media. They used $[(\eta^3\text{-allyl})Pd(Cl)]_2$ catalyst precursor, $P(m\text{-}C_6H_4SO_3Na)_3$ ligand, $Li[B(C_6F_5)_4{\cdot}2.5Et_2O$ (LiFABA) activator for the polymerization and obtained 89% conversion at 65°C over a period of 4 hours. The

M_w of the polymer was 1.03 million and the M_n was 384,000. Lipian claims that high catalyst activity was obtained with coordination of a phosphine to a cationic palladium center in the presence of the weakly coordinating FABA anion. Chemtob et al.[42] used the same catalysts, ligands, and activators as Lipian as well as a PCy_3 ligand to polymerize norbornene via mini-emulsion with hexadecane as a co-stabilizer. Chemtob obtained 100% conversion but could not measure the molecular weight of the polymer because it would not dissolve in any of the solvents they tried. In one experiment, they omitted hexadecane and the conversion still was 100% but the particle size was greater than 1 μm. The amount of coagulum was more than 20 wt%.

The goal of the present communication is to assess the possibility of producing stable polynorbornene latices with certain allyl palladium catalysts and to do so under conditions common to FR EP. Using *ab initio* batch emulsion polymerization conditions, we have studied the effect of Pd catalyst structure, the use of a lithium based activator, and the influence of catalyst, temperature, surfactant, and ionic strength levels. Where possible we comment on the apparent site of polymerization and the formation of the latex particles.

Results and Discussion

While the bulk of our experiments were carried out in latex form, we also used the catalysts and activator in solution polymerization to judge the inherent activity of the catalysts. The discussion below begins with this aspect of the work.

Solution Polymerization

Table 1 shows the recipe for these experiments conducted at 60°C and for a duration of 2 hours. For the TMP catalyst system, an optically clear and continuously increasing viscous solution was produced during the first hour. During the second hour, the solution turned slightly opaque indicating that some of the polymer had precipitated out of solution. The final conversion of monomer to polymer was only 60%. The DPP catalyst system resulted in a continuously precipitating polymerization process creating a completely gelatinous mass within the reactor while reaching 100% conversion. While the reaction rates were not measured directly, the visual aspects of the reactor contents indicated that the polymerization continued for much of the two-hour period. This set of experiments was our first indication that the polymer microstructure produced by the two different catalysts might be different enough to have contrasting solution properties.

The above experiments were repeated without the addition of activator and, as expected, no polymerization reactions occurred. This is to be contrasted with the results described in the next section.

Emulsion Polymerization

Our goal in this portion of the work was to contrast *ab initio* catalytic emulsion polymerization to that using the standard free radical process, albeit for a very different type of monomer. As such, we wanted to keep the sequence of addition of materials to the reactor the same and to study the effects of catalyst level, temperature, ionic strength, and surfactant level (and type) on the resultant latex characteristics. The following discussion is related to the results obtained for the first three variables. We will report a large study on the effect of surfactant type and level in a subsequent communication.

Catalyst and Surfactant Levels Used for Base Conditions

Both the TMP and DPP catalysts are activated by the removal of the chloride ion to form a vacant site. The LiFABA activator is used to abstract the chlorine as well as to leave the weakly coordinating FABA anion to associate with the palladium. Palladium has four bonds and the allyl group associates with two of them. Both the catalyst and the activator are soluble in water. The catalyst and activator concentrations were designed to yield a molecular weight of ~750,000 g/mole, assuming there would be one catalyst molecule per polymer chain (i.e., no chain transfer). This resulted in a catalyst concentration of 32 mg catalyst/L of water (6.7×10^{-5} M) for a 5% polymer solids latex. The molar ratio of palladium to lithium was normally 1:1, but we also performed experiments with no activator where the ratio was 1:0.

We chose to use sodium dodecyl sulfate (SDS) as the surfactant in this portion of the study and to add it at the level of 2.5 grams/liter of water. At 60°C, this represents a surfactant concentration just slightly below the cmc. We recognized that this would not enhance micellar nucleation of particles (if such a mechanism exists for catalytic emulsion polymerization). In addition, we performed all of the experiments in the batch mode of operation.

One of our initial concerns was the potential high sensitivity of the catalysts to degradation by oxygen. In standard FR EP, we are careful to exclude oxygen by purging the reactor after water addition with standard grade nitrogen gas, and usually remove oxygen from the water prior to adding it into the reactor. No other materials are de-oxygenated prior to adding them to the reactor, but we keep a slow flow of nitrogen to the reactor throughout the reaction. In our initial catalyst experiments, we swept the empty reactor with argon, cannulated de-oxygenated water to the reactor from a Schlenk flask using argon, purged the norbornene/acetone and surfactant/water solutions with argon and added both in the same manner as the water. We prepared the catalyst and activator solutions in a glove box, and injected them into the reactor. In contrast, we conducted additional separate experiments with both catalysts in which we used standard grade nitrogen gas and followed the procedure noted above for the "standard" FR EP, but maintained the injection of the catalysts and activator to the reactor. The results for these contrasting experiments are displayed in Table 2. It is seen that the extra care to exclude oxygen did not significantly affect the overall conversion levels, and the coagulum levels (a significant problem for many of the reactions described in this paper) showed no clear trend. Thus, it appears that the usual oxygen purging precautions employed in emulsion polymerization might also be applicable to such reactions using the catalysts of Figure 4. Nonetheless, we conducted most of the experiments reported below under the more stringent conditions.

Table 2. Oxygen sensitivity of norbornene emulsion polymerization

Experiment Number	wt% solids theoretical	wt% polymer in coagulum	% total conversion	Comments	
DEC2-60	5.3%	50%	73.0%	thorough O_2 purging	DPP catalyst
DEC2-85	5.1%	48%	69.9%		
DEC2-92	5.0%	34%	67.2%	moderate O_2 purging	
DEC2-96	5.0%	24%	70.1%		
DEC2-37	5.7%	30%	71.8%	thorough O_2 purging	TMP catalyst
DEC2-95	5.1%	31%	67.5%	moderate O_2 purging	
DEC2-97	4.9%	46%	67.1%		

Experiments with Variations in Catalyst/Activator Levels

The DPP catalyst concentration was varied to determine if the polymer conversion, the latex stability and the polymer molecular weight were affected by the amount of catalyst. The activator was also varied with the catalyst to keep with the molar ratio of palladium to lithium 1:1. For this series of experiments, the conversion and amount of coagulum are shown as a function of catalyst concentration in Figure 7. The conversion and coagulum data were quite reproducible. The overall conversion appears to increase somewhat with catalyst level until a concentration of about 120 mg catalyst/L. Continued catalyst concentration increases showed no further improvement in conversion level. In addition, as the conversion increased, the amount of coagulum decreased markedly, and the minimum amount of coagulum corresponded to the maximum conversion at 120 mg catalyst/L. The coagulum level markedly increased at a catalyst concentration of 325 mg/L. Although the catalyst and activator are both ionic, the combined ionic strength of the catalyst and activator is only 1.5x10^{-3}M. This ionic strength would have a negligible effect on colloidal stability in normal (i.e. free radical) styrene or acrylate latices.

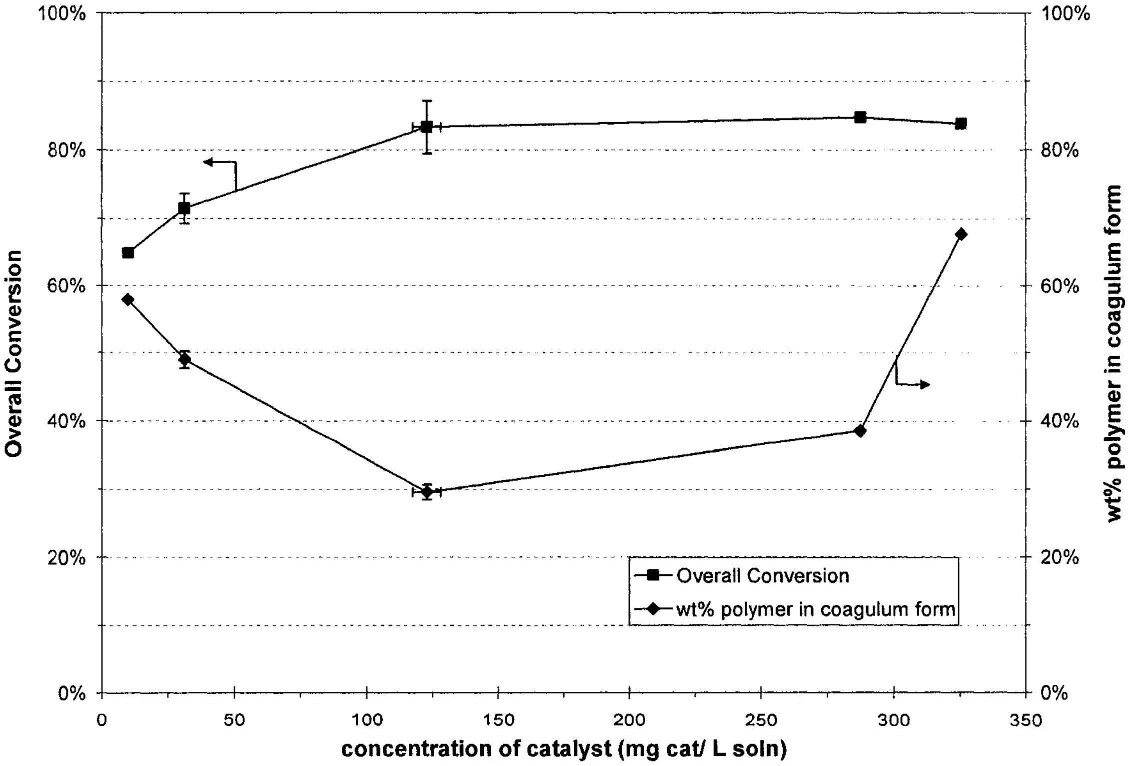
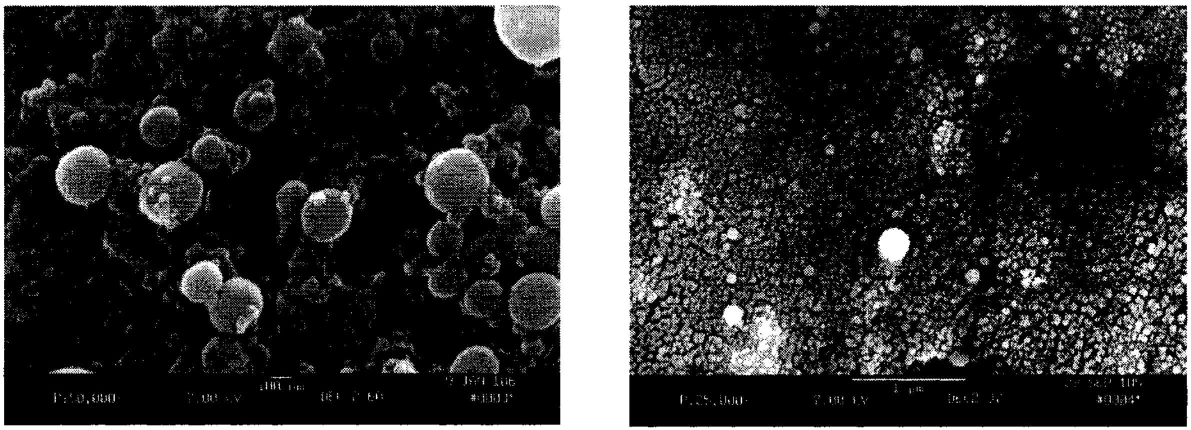


Figure 7. Overall polymer conversion versus catalyst concentration of norbornene polymerization at 60°C with DPP catalyst.

The T_g of polynorbornene is high (~300°C) and with the reaction temperature at 60°C, the Fox equation suggests that the highest conversion that should be attained before the glass effect prevents further polymerization is ~70%. At high catalyst concentrations, the theoretical conversion of 70% is surpassed and 80% conversion is experimentally attained. This implies that the glass effect does not limit the polymer conversion in the same manner that it does in free radical polymerization. This is surprising.

In these experiments we expected the polymer molecular weight to decrease as the catalyst concentration was increased. This assumes that there is one catalyst molecule per polymer chain. Decreasing the polymer molecular weight may increase the solubility of the polymer in solution. Polynorbornene did not dissolve in several solvents, even when produced at high catalyst concentrations. Others have also noted that polynorbornene does not dissolve in a number of solvents[34,42] while others note that it does[19,20,35]. The mentioned solvents (i.e., 1,2-dichlorobenzene, bromobenzene, cyclohexane) did not dissolve our polynorbornene and since we were not able to get polynorbornene in solution, there are no MW data to report at the present time.

The experiments with 32 mg catalyst/L of water yielded almost 50% and 30% coagulum with DPP and TMP catalyst, respectively. The resulting latex was examined via SEM and the results are shown in Figure 8a. The particle size contains mainly small particles around 30–80 nm and a few larger particles around 100–300 nm. Just as there were solubility differences between the two catalysts in solution polymerization, there is an apparent difference in the particle size distributions they created. There are fewer large particles when the TMP catalyst is used as seen in Figure 8b.



(a) (b)

Figure 8. SEM image of polynorbornene particles made via (a) DPP catalyst (scale bar equals 100 nm) and (b) TMP catalyst (scale bar equals 1000 nm), both with LiFABA activator.

Variations with Temperature

If the glass effect limits final conversion levels, then in the absence of competing effects, the conversion should increase slightly at higher temperatures and decrease slightly at lower temperatures. Figure 9 is a plot of polymer conversion versus reaction temperature over the range of 50–80°C for the standard polymerization recipe conditions listed in Table 1 using the DPP catalyst. The amount of coagulum drastically increased as the temperature increased; the instability occurred immediately after the activator was added to the reactor and worsened with time. Surprisingly, over the same temperature range, the overall conversion decreased slightly, again suggesting that the glass effect does not limit conversion in the same manner as in standard FR EP.

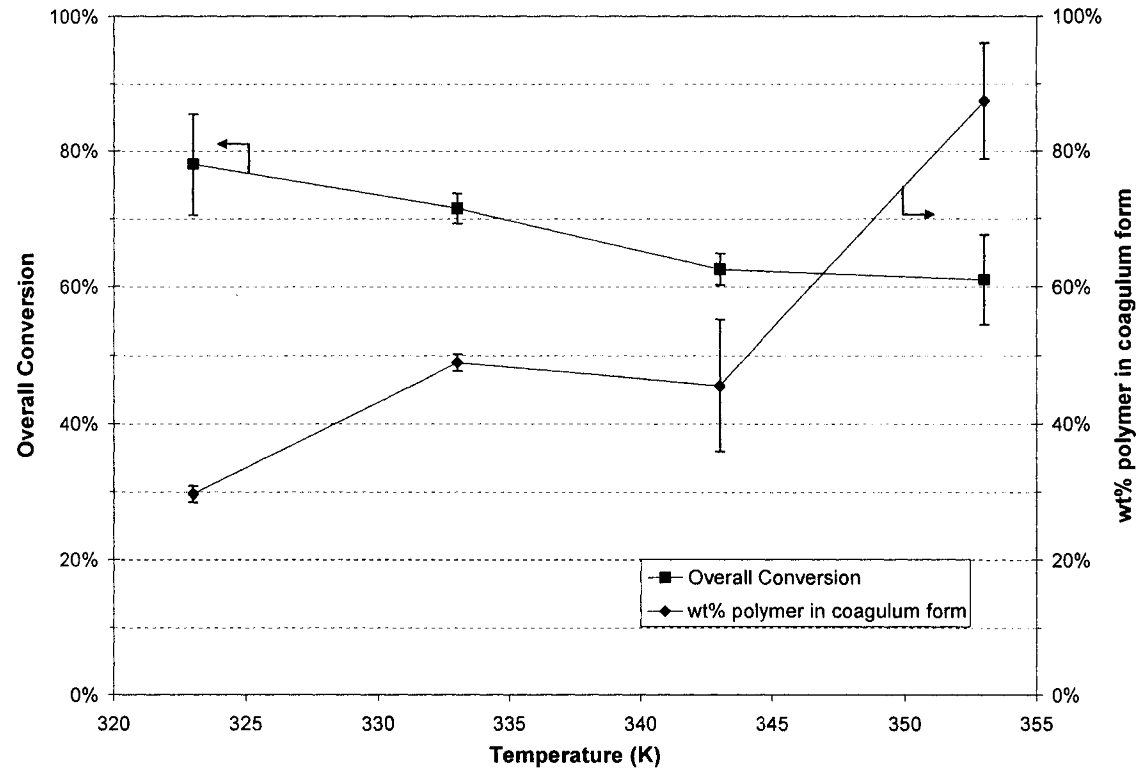


Figure 9. Overall polymer conversion versus reaction temperature of norbornene polymerization with DPP catalyst.

Ionic Strength Effects

Both the catalyst and the activator are ionic species. The lithium from the activator is thought to abstract the chloride from the catalyst, leaving a cationic vacancy on the catalyst[31]. The vacancy is weakly coordinated with the activator anion and is the site of polymerization. If the vacancy becomes too strongly coordinated, monomer will not easily access the vacant site and polymerization will be hindered or prevented. In this sense, we wondered if the overall ionic strength of the aqueous phase would affect the catalytic activity. Monovalent buffers, such as sodium bicarbonate, are frequently used in FR EP[14-16]. When there are too many ions in such emulsion polymerization systems, the polymer particles may destabilize and coagulate. In our study, we wanted to examine if the catalyst efficacy and the amount of coagulum would be affected by variations in ionic strength (using NaCl). Figure 10 is a plot of overall conversion and coagulum level as a function of the total salt level and takes into consideration the ionic strength that is contributed by the SDS. The latter is depicted by the shaded area on the plot. The polymer conversion initially increased with ionic strength, from 72% at 0.01M to 86% at 0.03M. Under the same conditions the coagulum level surprisingly decreased from 49% to 36%. This increase in polymer conversion was unexpected because we thought that the increased chloride ion concentration might interfere with the catalyst site. When the ionic strength was increased further to 0.07M, the overall conversion did decrease (back to the original level of 72%) while the percentage of coagulum slightly increased. Going further, the overall conversion decreased drastically at an ionic strength of 0.18M. Thus, it appears that there is a significant deleterious effect of salt content on the polymer conversion. Interestingly, the coagulum level seemed to have been relatively unaffected by the addition of NaCl.

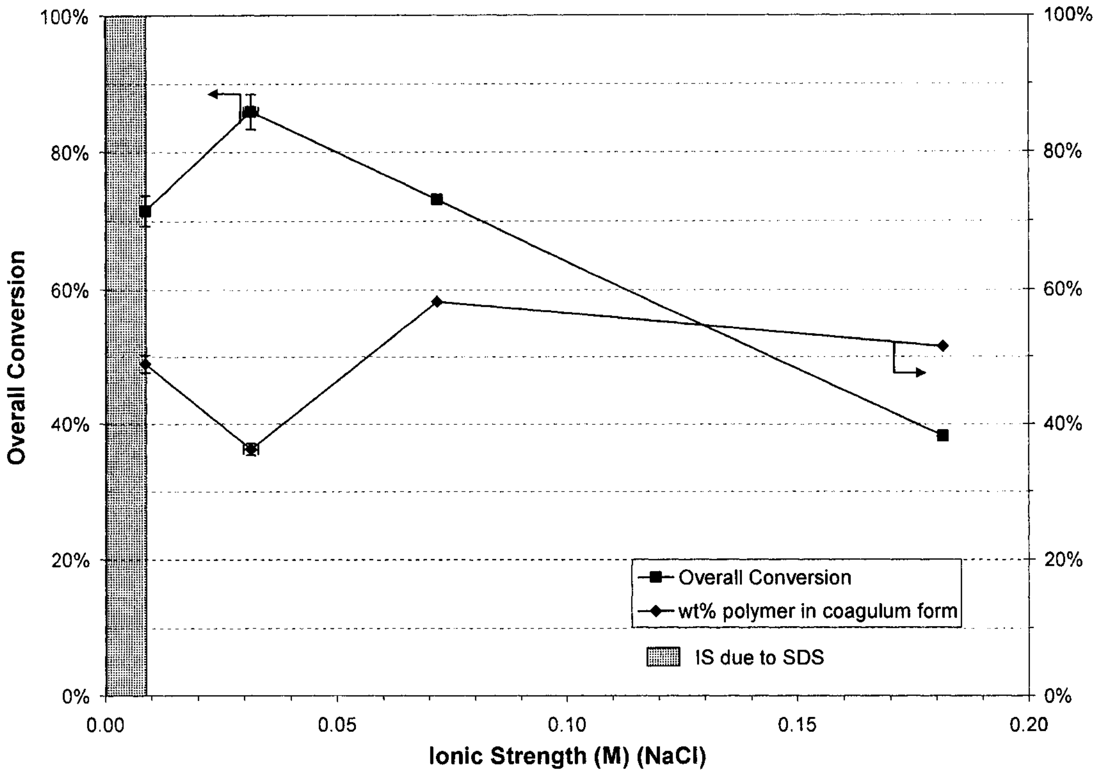


Figure 10. Overall polymer conversion versus ionic strength of norbornene polymerization at 60°C with DPP catalyst.

Experiments Without Activator

If the lithium ion in the activator is thought to abstract the chlorine from the catalyst to produce an active site, could something else activate the catalyst as well? To probe this question we were interested in seeing if the catalyst could be activated and polymerization achieved without the LiFABA activator. A series of emulsion polymerization experiments was conducted with the same concentrations of TMP catalyst and surfactant as Table 1, but without the activator. As previously noted, when the catalyst and activator were used together, the overall conversion was 72% and the coagulum level was 30%. The latex particle size distribution included small particles (50–100 nm) as well as a few larger particles (200–500 nm) as seen in Figure 8b. In contrast, when no activator was used, an overall conversion of 66% was obtained. Thus it appears that in this latex system it is not necessary to have the LiFABA activator to achieve reasonable polymerization. There was also a drastic decrease in the coagulum level to 4%, confirmed with replicate runs. This coagulum was markedly different in physical form than the coagulum formed with activator, as will be discussed later. The particle size distribution was limited to particles in the 30–70 nm diameter range as seen in Figure 11. While we did not accurately measure the rates of polymerization, we did find that those with activator present were faster (2 hours to completion) than those without activator (4 hours to completion).

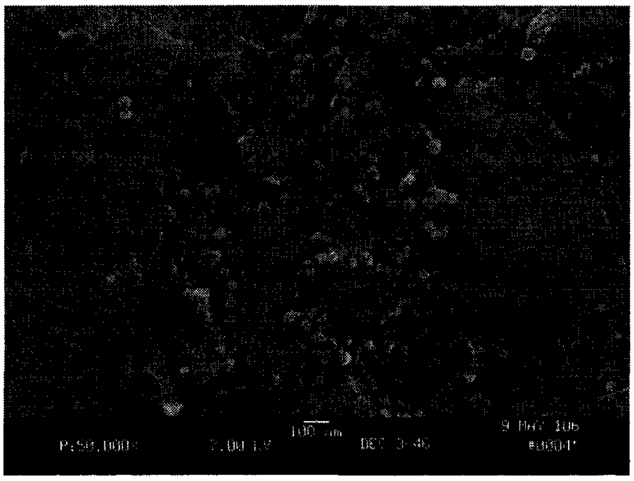


Figure 11. SEM image of polynorbornene particles using only TMP catalyst (no activator). Scale bar equals 100 nm.

Given the above results in emulsion polymerization, we tried the same reaction in solution polymerization. We again used the recipe in Table 1, and in this case, we got no polymerization at all - a result that we fully expected. Going a bit further, we tried the latex recipe without surfactant but with activator. In this case, we achieved "normal" conversion of about 76% but, as might be expected, we obtained essentially complete coagulum (93% of the polymer in coagulum form). Leaving the activator and the surfactant out of the emulsion polymerization recipe (thus having just water, monomer, and catalyst) resulted in no polymerization. Taken together these results offer clues as to the chemical reaction mechanisms involved in these experiments.

Competitive Reactions During Catalytic Emulsion Polymerization of Norbornene

Clearly, the amount of coagulum formed in most of the reactions described above is far greater than any acceptable value and certainly well above that commonly experienced in free radical based emulsion polymerizations. This led us to investigate the nature of the coagulum formed in the catalytic emulsion polymerization reactions via electron microscopy. A typical example is shown in the SEM image of Figure 12.

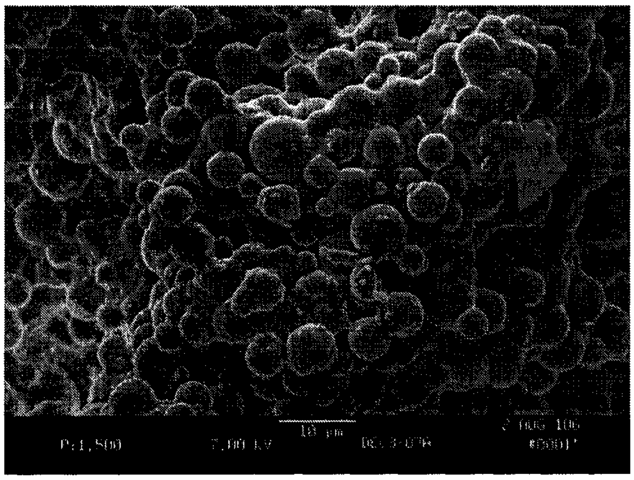


Figure 12. SEM image of the coagulum produced in the emulsion polymerization recipe of Table 1 with the TMP catalyst. Scale bar equals 10 μm.

It is very clear in this photo that the coagulum is composed of an agglomeration of polymer particles in the 10 μm diameter range. This is entirely consistent with the size of emulsified monomer droplets in normal free radical batch emulsion polymerizations that serve as reservoirs of monomer to supply the reactions that take place in the growing polymer particles (which are two orders of magnitude smaller than the emulsified droplets). Such coagulum forms to varying, but to very large degrees in all of the Cat EP reactions utilizing the activator described above. It does not form when we eliminate the LiFABA activator. Noting that we achieve roughly normal levels of overall conversion and the usual small latex particles without the use of activator, we now speculate that it is possible that the coagulum produced in systems utilizing the LiFABA activator results from the catalyst and activator migrating to the emulsified droplets and promoting rapid polymerization within them, much as in the solution polymerization reactions described earlier. Without activator present we know that polymerization does not take place in solution polymerization, nor in the bulk polymerization of the norbornene. It appears to us that without the LiFABA activator the catalytic emulsion polymerization takes place in the aqueous environment and creates latex particles in the 50 nm size range, and that these particles are stabilized by the SDS surfactant in the normal fashion. Considering the Cat EP experiment with neither activator nor SDS, which showed no polymer formation, it appears that the SDS surfactant may play a larger role than simply stabilizing particles. This leads us to further speculate that the allyl Pd catalyst is somehow activated by the SDS surfactant, perhaps acting as a weakly coordinating anion. We will comment more extensively on this in a future report.

Concluding Remarks

With the above thoughts, we reflect upon the overall results presented in this paper. It now appears to us that in the standard latex formulations expressed in Table 1, we create a situation in which there is a significant competition for reaction in distinctly different regions of the overall reaction medium. For batch emulsion polymerization reactions there is always that period of time in which reaction can take place in the aqueous phase and also possibly in the emulsified monomer droplets. In free radical emulsion polymerization, reaction in the large droplets is not important relative to the much faster reactions in the aqueous/micellar environment. However, in the catalytic emulsion polymerization of norbornene that appears not to be the case. Here we think that when the LiFABA activator is present, reaction happens in both the aqueous environment and in the large emulsified droplets – to an extent that nearly equal amounts of polynorbornene are produced in both places. When the activator is left out of the recipe, polymerization in the emulsified droplets is eliminated because catalytic reactions in those droplets require the presence of the LiFABA activator in order to create a vacancy on the Pd to induce polymerization. It appears that the LiFABA activator is not required to promote polymerization in the water and surfactant environment. Clearly, there are likely to be other complications to understanding the mechanisms of polymerization and especially latex particle formation that have not yet been addressed here, but the ideas presented above appear to us to be a start on that task.

CHAPTER 3

SURFACTANT EFFECTS IN THE *AB INITIO* POLYMERIZATION OF NORBORNENE

Abstract

The polymerization of olefins in aqueous media by late transition metal catalysts has created new opportunities to produce latex particles based on ethylene and its olefinic derivatives. In this work, we have concentrated on creating water-based latices from the strained cyclic olefin, norbornene. This has been done as *ab initio* batch emulsion polymerizations using allyl palladium catalysts and a lithium based activator, supported by a variety of surfactants. The role of surfactants in traditional emulsion polymerization is to assist in particle nucleation and/or to stabilize latex particles. We studied the role of several classes of surfactants in the emulsion polymerization of norbornene with Pd catalysts, both with and without the activator LiFABA. In the catalytic emulsion polymerization of norbornene, some of these surfactant classes were found to act as weakly coordinating anions with the Pd based catalysts to promote polymerization. When the base latex recipe already contains an activator specifically designed to work effectively with Pd in organic media (e.g. LiFABA), certain classes of surfactants (e.g. sulfates) act to provide an alternative pathway for polymerization and latex particle formation. Other surfactants (e.g. cationics) can actually suppress all or part of the polymerization by destructively interfering with either the catalyst or the separately added activator. Alkyl sulfates and sulfonates were both effective activators of allyl Pd catalysts and produced latex particles (ca. 40–50 nm) without significant amounts of coagulum. This activity is significantly dependent on the alkyl chain length,

and alkyl sulfate anions are more active than the equivalent alkyl sulfonate anions. Cationic, fatty acid and non-ionic surfactants produced variable, but ineffective, results in our studies.

Introduction

The polymerization of olefins using late transition metal catalysts in aqueous emulsions is possible and has begun to receive some attention in the literature[4-13]. For the most part, these studies have utilized the mini-emulsion polymerization route and often used substantial amounts of hexadecane to retard Ostwald ripening of the particles during polymerization. In those studies reported thus far, sodium dodecyl sulfate (SDS) has been the main surfactant employed, with Chemtob et al.[42] examining four other surfactants, but using SDS for the bulk of the experiments. Regarding the emulsion polymerization of norbornene and its derivatives, very few studies have been reported. Puech et al.[39] were the first to report the aqueous polymerization of norbornene via vinyl polymerization. Their catalyst was $PdCl_2$ and produced low molecular weight oligomeric polynorbornene. They found that an increase in their surfactant (SDS) level increased the molecular weight of the polymer and that the latex particles formed were only 10–20 nm in diameter. Lipian et al.[31] reported the polymerization of butyl-norbornene in aqueous media using $[(\eta^3\text{-allyl})Pd(Cl)]_2$ catalyst precursor, $P(m\text{-}C_6H_4SO_3Na)_3$ ligand, and LiFABA activator with SDS as surfactant. They claimed that high catalyst activity is obtained with coordination of a phosphine to a cationic palladium center in the presence of the weakly coordinating FABA anion. Chemtob used the same catalysts, ligands, and activators as Lipian, as well as a PCy_3 ligand, to polymerize norbornene via mini-emulsion with hexadecane as a co-stabilizer and SDS as surfactant. Chemtob could not measure the molecular weight of the polymer because it would not dissolve in any of the solvents they tried. When they omitted the hexadecane, they reported that the conversion was still 100% but the particle size was greater than 1 μm. The amount of coagulum was more than 20 wt%.

We have recently reported some results from our study on the *ab initio* batch emulsion polymerization of norbornene using two Pd based catalysts[1]. In that paper we concluded that there is a major competition for polymerization reactions between the latex particles (on the order of 50 nm in diameter) and the emulsified droplets (ca. 10 μm in diameter). The use of a Li borate activator (LiFABA) promoted polymerization in both the emulsified droplets and the aqueous phase – the former produced great amounts of coagulum and the latter produced stable latex particles. When using SDS as the surfactant, we achieved overall conversion levels of about 75% and about half of the polymer was produced as coagulum. The coagulum was identified as massive agglomerates of ~10 μm particles and thought to have come from reaction in the emulsified droplets. In an attempt to reduce/eliminate the coagulum in these latices we subsequently varied the type of surfactant used in the basic recipe and studied the resultant reactivity, overall conversion and coagulum levels. Anionic, cationic, and non-ionic surfactants were used alone and in combinations. The purpose of this chapter is to report those results for norbornene monomer and to comment on the possible mechanisms of polymerization and particle formation as they are affected by the surfactants employed in the recipe.

Results and Discussion

A useful backdrop for this discussion is to describe the set of reaction mechanisms that we proposed in our recent paper[1]. There we suggested that with either the TMP or the DPP catalysts in the presence of LiFABA activator there is an opportunity to have stable latex particle formation and simultaneously have reaction in the large, emulsified droplets. The latter leads to massive agglomerates of ca. 10 μm particles and the formation of coagulum. In the beginning our testing of a large number of surfactants arose from our desire to eliminate the coagulum, and ultimately, we have begun to gain a more complete picture of the role of surfactants as either positively or negatively interacting with the catalysts and/or the LiFABA activator. Figure 13 shows that when SDS is used (this was our "reference" surfactant against which to judge the performance of others) there may be three mechanisms responsible for the polymerization. The first is the migration of the catalyst and the LiFABA activator through the water and into the emulsified droplets to produce large polymer particles (eventually coagulum), and the second is to have the same catalyst and activator produce colloidally stable latex particles (ca. 40 nm in size). A third possibility is that of the surfactant acting as a weakly coordinating anion and activating the catalyst in the water phase leading to latex particle formation. These pathways numbered 1–3 and are depicted by the various arrows in Figure 13. These reaction steps are meant to be occurring simultaneously. It appears to us that the final characteristics of the latex are determined by the dominant reaction pathway that is specific to the recipe and temperature conditions used in the experiment. Indeed, our goal eventually became to influence the competition between the various potential mechanisms.

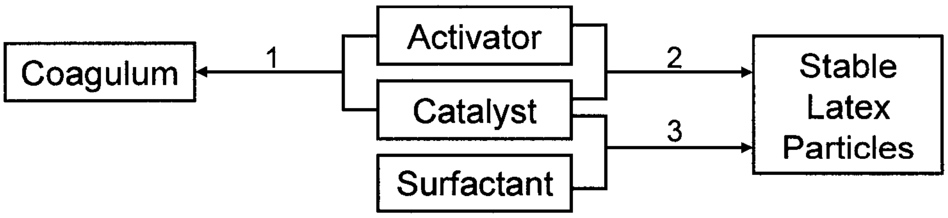


Figure 13. Proposed reaction pathways for norbornene polymerization using DPP or TMP catalysts with LiFABA activator.

Another interesting reference point is that of a latex recipe without any surfactant at all. Standard emulsification of monomer in water using mechanical stirring produces droplets around 10 μm or greater in diameter. When the catalyst and activator were sequentially added to our reactor containing only water and dispersed monomer, a rapid reaction ensued and an overall conversion of 70% was obtained. However, 92% of that polymer was in coagulum form, although there was a small amount (ca. 6%) of latex conversion. The stable latex particles had a broad size distribution of 50–300 nm. This indicates that there was some water phase polymerization even without the presence of surfactant. It now becomes interesting to observe what happens as various surfactants are added to the recipe, both with and without the LiFABA activator.

For discussion purposes, the surfactants are separated into classes; sulfates, sulfonates, cationic, fatty acid soap, and non-ionics. The overall polymer conversion resulting from the use of various surfactants can be found in Table 3. All of the experiments using LiFABA activator employed the DPP catalyst. The set of experiments that did not use the LiFABA activator used the TMP catalyst. The polymers produced were not soluble in a number of different solvents, and thus we were not able to obtain molecular weight data for any of the experiments at this time.

Table 3. Overall polynorbornene conversion as a function of surfactant type using DPP catalyst and LiFABA activator. The nonionic surfactants were added at the same masses, while the remaining surfactants were added at ~9X10^{-3} M in water.

	Experiment Number	wt% solids theoretical	wt% polymer in coagulum form	% overall conversion	[Surfactant] x10^{-3} (mol/L)	Surfactant
a	DEC2-70	4.7%	92%	76.0%	0.00	no surfactant
b	DEC2-62	5.0%	83%	16.3%	9.21	DBSA
	DEC2-63	5.3%	33%	35.1%	6.60	Aerosol OT
	DEC2-66	5.6%	33.%	64.1%	9.02	sodium hexadecane sulfonate
c	DEC2-73	5.5%	81%	57.9%	16.7	Igepal CO-520 (5EO Units)
	DEC2-75	4.6%	54%	30.2%	8.08	Igepal CO-520 w/8x10^{-3}M SDS
	DEC3-18	5.4%	23%	10.1%	8.63	Igepal CO-720 (12 EO Units)
	DEC3-14	5.3%	30%	15.4%	3.18	Igepal CO-890 (40 EO Units)
	DEC3-15	5.0%	19%	26.7%	2.06	Igepal CO-890 w/8x10^{-3}M SDS
	DEC2-74	4.7%	5%	11.1%	1.29	Igepal CO-997 (100 EO Units)
	DEC2-76	4.8%	81%	43.9%	0.86	Igepal CO-997 w/8x10^{-3}M SDS
d	DEC2-80	4.7%	31%	2.0%	7.89	CTAB
e	DEC2-55	5.1%	0%	0.0%	8.59	Sodium Stearate
	DEC2-57	5.0%	0%	0.0%	8.59	Sodium Stearate + TSPP
f	DEC2-59	5.3%	36%	59.5%	9.58	Rhodapex CO-436
	DEC2-60	5.3%	50%	73.0%	9.40	SDS (C-12)
	DEC2-85	5.1%	48%	69.9%	8.89	SDS (C-12)
	DEC2-69	5.4%	81%	74.0%	8.94	SDecS (C-10)
	DEC2-64	4.8%	34%	79.4%	8.58	STDS (C-14)
	DEC2-67	5.3%	24%	86.7%	8.85	STDS (C-14)
	DEC2-79	5.0%	11%	79.9%	8.41	SHDS (C-16)
	DEC2-82	5.2%	8%	81.1%	8.12	SHDS (C-16)
	DEC2-68	5.0%	31%	70.1%	7.90	SODS (C-18)

a – no surfactant, b – sulfonated series, c – non-ionic series, d – cationic, e – stearate, f – sulfate series, * EO – ethylene oxide

Sulfate Series

Since SDS, in the presence of our catalysts and activator, was able to enhance the production of latex particles and provide a new pathway that can effectively compete with reaction pathways 1 and 2 in Figure 13, we suspected that other alkyl sulfate surfactants would provide interesting results. Our conclusion that the alkyl sulfate anion provided a weakly coordinating pair with the Pd cation is supported by the work of Lapinte et al[46]. They used $PdCl_2$ as the catalyst to polymerize octene in aqueous emulsion and determined that the alkyl (C-12) sulfate anion coordinated with the Pd cation to effect the polymerization of the octene. Although our Pd catalyst is different, it appears to also be activated by the same sulfate anion.

Our first experiment utilized sodium sulfate, Na_2SO_4, salt instead of surfactant to test the unlikely possibility of the simple sulfate anion coordinating with the Pd cation to activate the catalyst without the LiFABA activator present. It did not do so, as no polymer was formed when LiFABA was absent. As previously mentioned, 'normal' 70% conversion was obtained when no surfactant was added and catalyst and activator were present. The Na_2SO_4 salt without activator yielded no polymer, which is similar to the experiment where no surfactant or activator was used.

We then used sodium alkyl sulfates of varying carbon chain lengths, ranging from 10 to 18 carbons. Figure 14 shows the results for sodium alkyl sulfates when LiFABA was used, and Figure 15 displays similar data for the experiments in which the LiFABA was omitted from the recipe. Figure 14 uses the DPP catalyst and Figure 15 uses the TMP catalyst. As we showed in a previous paper[1], the overall polymer conversion does not change when changing the catalyst. In Figure 14 it is striking to see as the alkyl chain length increased from 10 to 18 carbons that the conversion levels changed little while the coagulum levels dropped dramatically. This means that reaction pathway 3 became more and more prevalent with the increasing alkyl chain length and provided a highly competitive alternative to pathways 1 and 2 for polymerization. The C-16 alkyl sulfate effectively eliminated the tendency of the catalyst and the LiFABA to migrate to the large emulsified droplets and produce coagulum by providing a more rapid pathway for polymerization to produce small latex particles (ca. 40 nm). This interpretation of the results is supported by the fact that when the LiFABA is omitted of the recipe (Figure 15), there is very little coagulum formed and monomer conversion is nearly as high as it was when the LiFABA activator was present to offer an additional pathway for polymerization. Also in Figure 15, it is seen that the C-10 alkyl sulfate surfactant does not appear to activate the catalyst. This is apparently why this surfactant allowed the LiFABA to induce the formation of massive amounts of coagulum, as seen in Figure 14. It is striking that adding 2 methylene groups to this alkyl chain, so as to produce SDS, results in a dramatic increase in the activity of the catalyst.

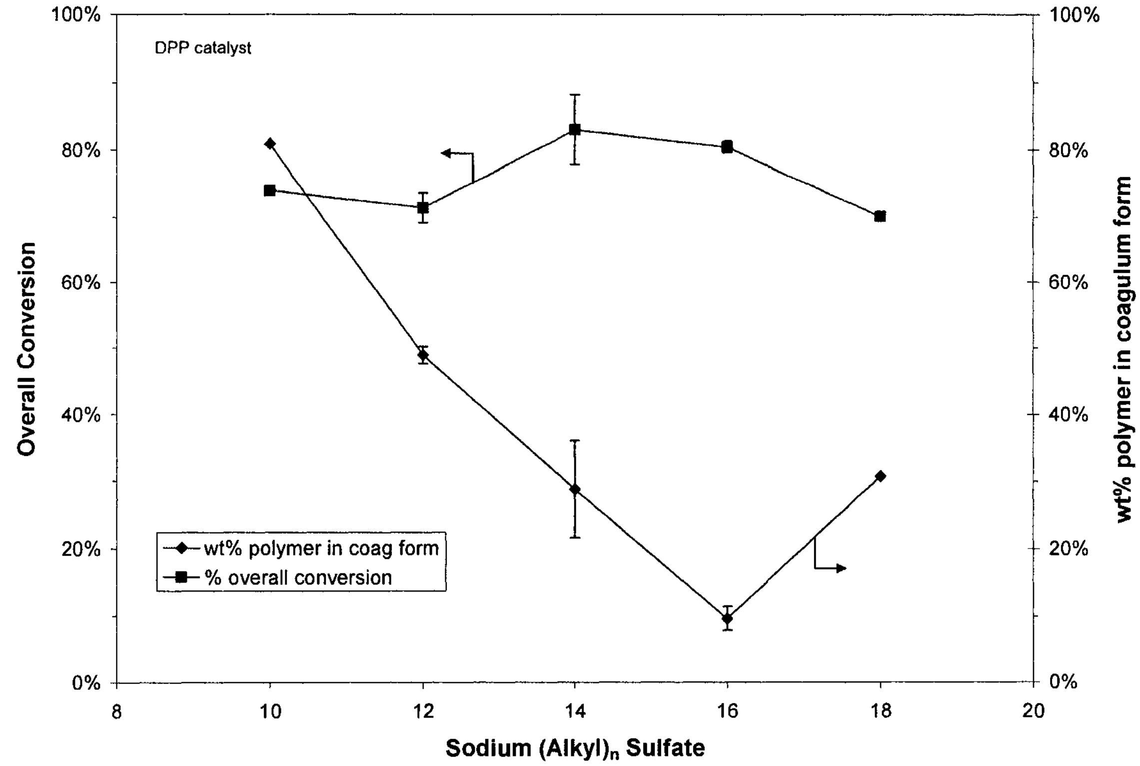


Figure 14. Overall polymer conversion of norbornene and coagulum level versus alkyl chain length (n= number of carbons in alkyl chain) of sodium sulfate surfactants for polymerization at 60°C with DPP catalyst and with LiFABA activator.

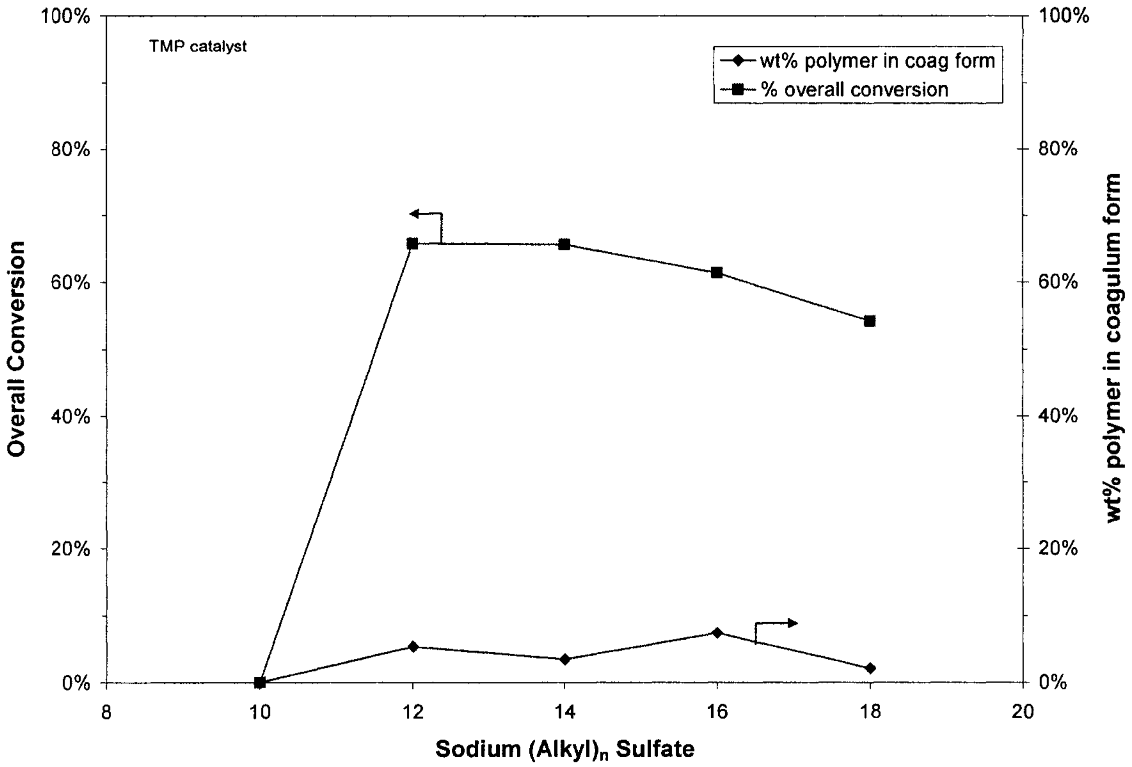


Figure 15. Overall polymer conversion of norbornene and coagulum level versus alkyl chain length of sodium sulfate surfactants for polymerization at 60°C with TMP catalyst (without LiFABA activator).

It appears from the data in Figure 14 and Figure 15 that the positive trend seen with increasing the alkyl chain length does not extend beyond 16 carbons, as the C-18 sulfate surfactant seems to perform less well than the C-16 surfactant, both with and without the LiFABA activator. In a further test of the effect of the characteristics of the organic portion of the sulfate surfactant, we chose to use an ammonium salt of nonyl phenyl ethylene oxide (4 units) sulfate (Rhodapex CO-436) in experiments with and without the LiFABA activator. As seen in Table 3, the monomer conversions using Rhodapex CO-436 was the lowest in the sulfate series, although the surfactant clearly activated the catalyst (i.e. when the Rhodapex CO-436 was used without activator, 40% overall conversion was achieved, indicating that the surfactant can activate the catalyst). Since the number of carbons in this surfactant is 23, it may be that it is too large to be as effective as the C-16 sulfate. On the other hand, it may be that the ethylene oxide group adds an additional hydrophilic nature to the surfactant and in that way alters the association with the Pd catalyst.

Lastly, there was no correlation found between the latex particle size and the alkyl chain length. All of the experiments contained small particles around 30–80 nm as well as a few larger particles around 100–300 nm, irrespective of the surfactant. The coagulum produced with the LiFABA was composed of agglomerates of ~10 μm particles and had a very different character than the small amounts of coagulum formed without LiFABA. The latter had the features of "normal" latex coagulum as usually found around the stir shafts and blades in latex reactors.

Sulfonate Series

Three surfactants were examined within the sulfonate series; sodium hexadecane sulfonate, dodecyl benzene sulfonic acid (DBSA), and Aerosol OT. These were chosen in an attempt to reduce the coagulum levels produced in reactions containing the LiFABA activator. They also serve to compare sulfonate surfactants to sulfate surfactants as potential weakly coordinating anions activating the Pd catalysts. Surprisingly the overall conversions obtained in these three surfactant experiments (Table 3b) were considerably lower than the surfactant free experiment. Sodium hexadecane sulfonate yielded the highest overall conversion at 64% with about one third of that in coagulum form. The polymer formed with DBSA was mainly produced as coagulum while the polymer formed with Aerosol OT had considerably less coagulum and a higher overall conversion level. Clearly these surfactants have affected the relative importance of the different pathways depicted in Figure 13. Sodium hexadecane sulfonate, similar to the C-16 sulfate except for the removal of an oxygen, yielded a total polymer conversion of 64%, with about a third of polymer in coagulum form. This is a decrease compared to C-16 sulfate which yielded 80% overall conversion. When the C-16 sulfonate was used without activator, 56% overall conversion was obtained (not shown in table). This indicates that the surfactant is able to activate the catalyst on its own. Both the C-16 sulfate and sulfonate experiments without activator yielded similar overall reactions; 61% and 56%, respectively. This suggests a shift towards the enhancement of reaction pathway 3, but without the total diminution of the pathway to coagulum formation (when the activator is used).

The DBSA significantly hindered the polymerization because there was only 16% overall conversion. Since the surfactant is present in large molar excess of both the catalyst and the LiFABA activator, destructive interference with either or both could totally destroy the reactivity of the system. Achieving 16% conversion with nearly the entire polymer in coagulum form would suggest that pathway 1 in Figure 13 has been seriously diminished (as compared to the experiment with no surfactant) without any significant positive effect on the other two reaction pathways. Aerosol OT yielded a slightly higher conversion of 35% compared to DBSA with significantly less polymer in coagulum form, 33%. This result suggests to us that pathway 3 has been enhanced at the expense of pathway 1 for this surfactant but the activity of the catalyst has decreased.

Cationic

Cetyl trimethyl ammonium bromide (CTAB) was the only cationic surfactant used. The conversion level for the CTAB experiment was only 2%. Bromide is the anion of this surfactant and it is very unlikely that it can act as a weakly coordinating anion with the catalyst. Pathway 3 in Figure 13 is not active as confirmed by Lapinte et al.[46] who used a brominated cationic surfactant with $PdCl_2$ catalyst. Clearly the CTAB had a catastrophic effect on the reactivity of our catalyst/activator system and even prevented this pair from migrating to the large emulsified droplets to produce polymer. We conclude that the cetyl trimethyl ammonium cation interferes with the LiFABA anion of the activator and effectively shuts down reaction pathways 1 and 2 in Figure 13, without providing an alternative pathway to polymerization.

Stearic Acid Soap

When we used sodium stearate as surfactant, we did so with and without the use of tetrasodium pyrophosphate buffer (TSPP). TSPP buffers the system at a pH of 9.0 – without it the system operated at a pH of about 6, somewhat above the pKa of the carboxylic acid group[47]. Absolutely no reaction was observed when using this surfactant with or without TSPP. Clearly the reaction pathways 1 and 2 must have been eliminated by the C-16 alkyl carboxylic anion. We suspect that this anion interacted with the Pd cation in a manner such that it eliminated the catalyst's ability to coordinate with the LiFABA. Since the molar concentration of the surfactant was so much higher than that of the catalyst, a strong, negative interaction with the catalyst would remove the catalyst from the system and eliminate any possibility of polymerization. Even without the TSPP, it would appear that the carboxylic group is ionized enough to interfere destructively with the catalyst.

Non-Ionic Series

Four nonyl-phenyl ethylene oxide surfactants were used with various ethylene oxide chain lengths. These non-ionics were tested alone as well as with SDS. The polymer conversion and coagulum levels achieved with these surfactants are listed in

Table 3c. These data are more dramatically summarized in Figure 16 where the conversion and coagulum levels are plotted as a function of the ethylene oxide (EO) chain length. We had expected that the non-ionic surfactants might stabilize the particles that were formed without interfering with the polymerization reactions, but the data tell a very different story. As seen in Figure 16, the surfactant with 5 EO units produced slightly less polymer than the "no surfactant" experiment but again with nearly the entire polymer produced in coagulum form. Additional EO units resulted in a dramatic decrease in the conversion levels to 10%, but the vast majority of the polymer was created as stable particles. By referring to the reaction pathways in Figure 13 we suggest that these non-ionic surfactants may render the LiFABA activator to be inactive (as evidenced by essentially no coagulum formation) while slightly activating the catalyst to promote some limited latex conversion and the formation of stable latex particles. This apparent activity with low conversion level is consistent with that seen by Lapinte with the use of Bri J 35 ($CH_3(CH_2)_{11}(OCH_2CH_2)_{23}OH$), a non-ionic surfactant.

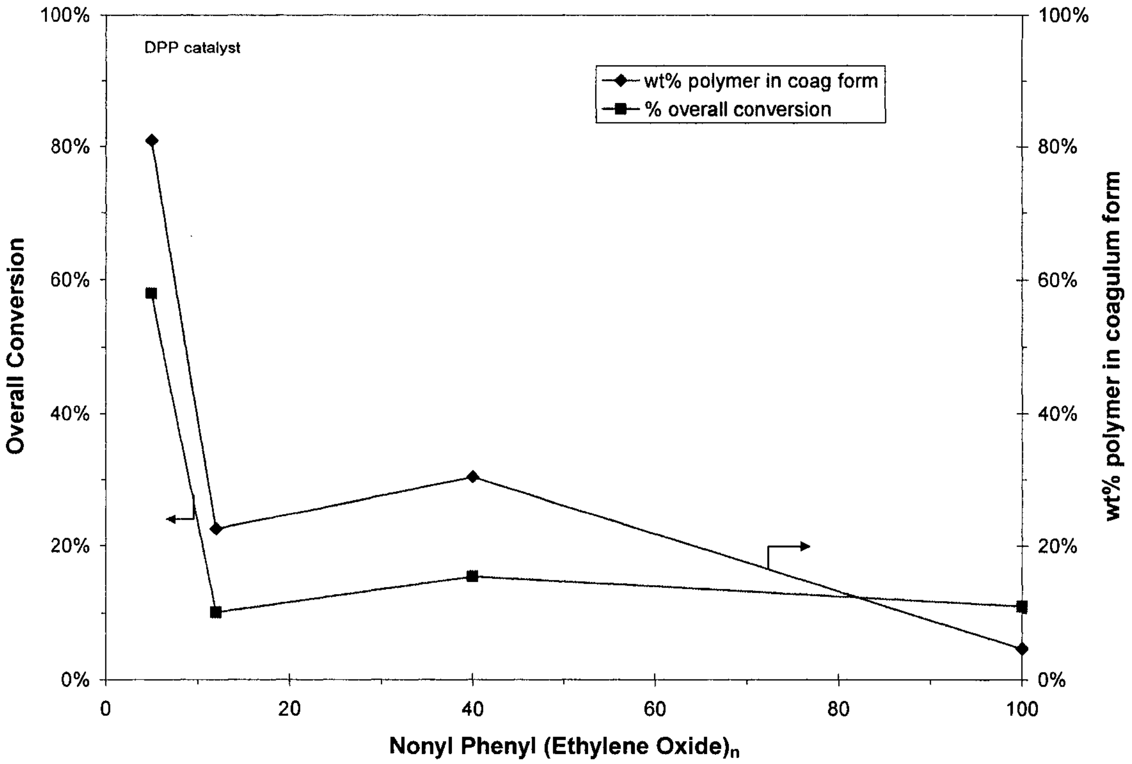


Figure 16. Overall polymer conversion and coagulum level versus ethylene oxide chain length of nonyl phenyl surfactant for norbornene polymerization at 60°C with DPP catalyst and with LiFABA activator.

Also entered into Table 3c are some results using a dual surfactant system by adding SDS to several of the non-ionic surfactants (those with 5, 40 and 100 EO units). We had anticipated that we might achieve at least the quality latex production obtained with SDS alone and perhaps some further enhancement due to the additional surfactant. The results are quite perplexing. At the 5 EO chain length, the two surfactants working together reduced the overall conversion level from that achieved with just the non-ionic alone (30% vs. 58%), yet also reduced the portion of the polymer produced as coagulum (55% as compared to 81%). When the same amounts of SDS were added to the non-ionic surfactant with 40 and 100 EO units, the conversion levels were 27% and 44%, respectively; both results were improvements over those obtained with just the non-ionic surfactant alone. However the effect on the coagulum formation in these two experiments showed opposite trends. Thus we see no consistency in the overall results of the non-ionic surfactant study and do not offer any suggestions as to possible effects on the reaction pathways displayed in Figure 13.

Concluding Remarks

It is clear to us that a number of surfactants commonly used in standard emulsion polymerization of vinyl monomers can serve as weakly coordinating anions for Pd based catalysts used to polymerize norbornene in aqueous emulsion. Both alkyl sulfate and alkyl sulfonate salts provide significant to excellent activation of the two forms of Pd catalysts used in our study. Additionally, there is a strong effect of the alkyl chain length on this activation capability when the number of carbons is less than 12, and some indication that the activation decreases as the number of carbons is greater than 16. The alkyl sulfate anions appear to be better activators than the alkyl sulfonate anions. When using such surfactants, it is not necessary to provide other means of activation of the Pd catalyst such as commonly done by the use of LiFABA. Cationic and fatty acid surfactants destructively interfere with the LiFABA activator and the Pd catalyst, respectively, and it is not clear why neither class of these surfactants was useful in suppressing the coagulum formation while allowing polymerization. The non-ionic surfactants create a complicated set of interactions with either or both of the catalyst and LiFABA activator, but do not provide for an overall effective stabilizing system. The role of the surfactant in activating the catalyst in norbornene emulsion polymerization sets it in striking contrast to the traditional role of the surfactant in standard, free radical emulsion polymerization where the surfactant can serve to nucleate and then stabilize the latex particles, but it does not influence the inherent activity of the initiator.

CHAPTER 4

AB INTIO POLYMERIZATION OF NORBORNENE DERIVED MONOMERS

Abstract

The use of late transition metal catalysts for the polymerization of olefins in aqueous media has created new opportunities to produce latex particles based on ethylene and its olefinic derivatives. In this work we report on the production of water based latices from a variety of monomers based on the strained cyclic olefin, norbornene. These have been carried out as *ab initio* batch emulsion polymerizations using allyl palladium catalysts and a lithium borate activator, as well as sodium dodecyl sulfate surfactant. We find that the n-alkyl norbornenes can be polymerized in aqueous emulsion and that the mechanisms for latex particle formation are the same as that for norbornene monomer alone. The latex particles created are small, averaging about 45 nm in diameter. As in the case of norbornene, large amounts of coagulum can be formed if the catalyst and activator are allowed to reach the emulsified monomer droplets and effect polymerization in that location. As the substituents on the norbornene become larger and non-polar, it is necessary to consider their effect on the water solubility of the monomers in order to analyze the experimental results in an effective manner. Our studies included butyl and decyl norbornene, vinyl and butenyl norbornene, and methanol norbornene.

Introduction

In two recent papers[1,2] we have described some of our studies on the catalytic emulsion polymerization of norbornene. In particular, we used two forms of allyl palladium chloride catalysts and an activator, LiFABA, a fluorinated borate. The chemical structures of these compounds have been detailed elsewhere[1,2] and they function by forming an ion pair. This activation is strong in organic media and quite weak in an aqueous phase. Nevertheless, water does not deactivate the catalysts as evidenced by the rapid reaction of norbornene when the monomer is simply dispersed in water without a surfactant and the catalyst and activator are added to the aqueous phase. It appears that the Pd catalyst and LiFABA activator can migrate through the water to polymerize the norbornene in the dispersed droplets of about 10 μm in diameter[1]. This produces massive coagulum formation. When surfactants are added, as in standard emulsion polymerization, several different things happen depending on the type of surfactant used. In particular, the alkyl sulfate surfactants can act as weakly coordinating anions and activate the catalyst in the water so that small latex particles (~40 nm) are formed. Without the addition of LiFABA to the emulsion, conversion of norbornene at 60°C reaches 70+% and little or no coagulum is formed[2]. When the LiFABA activator and the alkyl sulfate surfactants are present at the same time, there appears to be a competition for the activation of the catalyst by the LiFABA and by the surfactant. Such conditions produce variable ratios of coagulum to stable latex particles depending on the particular surfactant used, with the hexadecyl sulfate surfactant resulting in almost no coagulum.

In the above manner, we have investigated the effects of catalyst level, temperature, ionic strength, and surfactant type on the production of polynorbornene latices[1,2]. We now extend our report to include a variety of substituted norbornene monomers. These studies were carried out in both organic solutions and in aqueous emulsions using the same catalysts and activators (LiFABA and surfactants) as described above. The monomers were all derivatives of norbornene with substitutions at the 5th position and included the butyl and decyl alkyl derivatives, the vinyl and butenyl derivatives, and the methanol derivative, as shown below in Table 4. The reactivity of a number of these monomers has been studied by others in solution[28,30-32,40] as well as emulsion[31,42] polymerization using other Pd based catalysts and then compared to the reactivity of norbornene. Because these monomers are commonly prepared via Diels-Alder reactions, such functionalized norbornenes consist of both *exo* and *endo* isomers[48]. Often the ratio of the *exo* to *endo* isomers is in the range of 25:75[32], and it has been shown[42,48,49] that the *endo* form is moderately to substantially less reactive that the *exo* form. The purpose of our homopolymerization studies was also to compare the reactivities obtained with these monomers to that of norbornene itself, but in this case using aqueous emulsion polymerization systems. In addition we were interested in whether or not the same mechanisms of reaction and latex particle formation were apparent for these substituted norbornene monomers as those found for norbornene.

Results and Discussion

Solution Polymerization

Solution polymerizations were performed with three of the monomers to gauge their activity with the catalyst and what we presumed would be their maximum conversion levels. The reactions were performed in cyclohexane at 60°C for a period of two hours. The three monomers were norbornene (NB), 5-butyl-2-norbornene (NB-4), and 5-decyl-2-norbornene (NB-10). The results of the polymerizations of these monomers can be found in Table 4 and Figure 17. Both TMP and DPP catalysts were used and the DPP catalyst with NB resulted in a continuously precipitating polymer that created a gelatinous mass within the reactor while reaching 100% conversion. The TMP catalyst with NB resulted in a viscous, opaque solution that only reached 57% conversion in the two hours of reaction. The visual differences between the resulting solutions, as well as the polymer conversion, indicates that there may be a difference in polymer microstructure dependent on the catalyst used. Neither the butyl nor decyl norbornene exhibited such a dramatic visual or conversion differences between catalysts.

Table 4. Monomer conversions and observations from solution polymerizations of various monomers using either TMP or DPP catalyst with LiFABA activator in cyclohexane at 60°C

Experiment Number	wt% solids theoretical	% total conversion	Monomer	Catalyst	Observations	M_W (g/mole)	M_N (g/mole)	M_W/M_N
DEC3-25	5.1%	100.0%	NB	DPP	precipitated	Insoluble in chloroform		
DEC3-26	5.2%	56.8%	NB	TMP	opaque	554,523	373,008	1.49
DEC3-27	5.1%	7.2%	NB-4	DPP	clear	284,651	119,867	2.37
DEC3-28	4.9%	8.3%	NB-4	TMP	clear	408,980	244,388	1.67
DEC3-29	5.1%	33.6%	NB-4	4x DPP	clear	----	----	----
DEC3-30	5.3%	38.8%	NB-4	4x TMP	clear	Insoluble in Chloroform		
DEC3-23	5.1%	78.2%	NB-10	DPP	clear	267,393	134,223	1.99
DEC3-24	5.2%	98.6%	NB-10	TMP	clear	Insoluble in Chloroform		

The polynorbornene formed using the DPP catalyst was a gelatinous mass which would not dissolve in chloroform. The polymer formed with the TMP catalyst dissolved in chloroform and the molecular weight determined by GPC was 555,000 g/mole. The expected molecular weight of the polymer, assuming one Pd atom per polymer chain and complete monomer conversion, is 750,000 g/mole. This molecular weight is slightly lower than the theoretical, potentially indicating that all of the catalyst is not active. At the present time, molecular weight data range from 250,000 to 550,000 g/mole, with some polymers not soluble in chloroform.

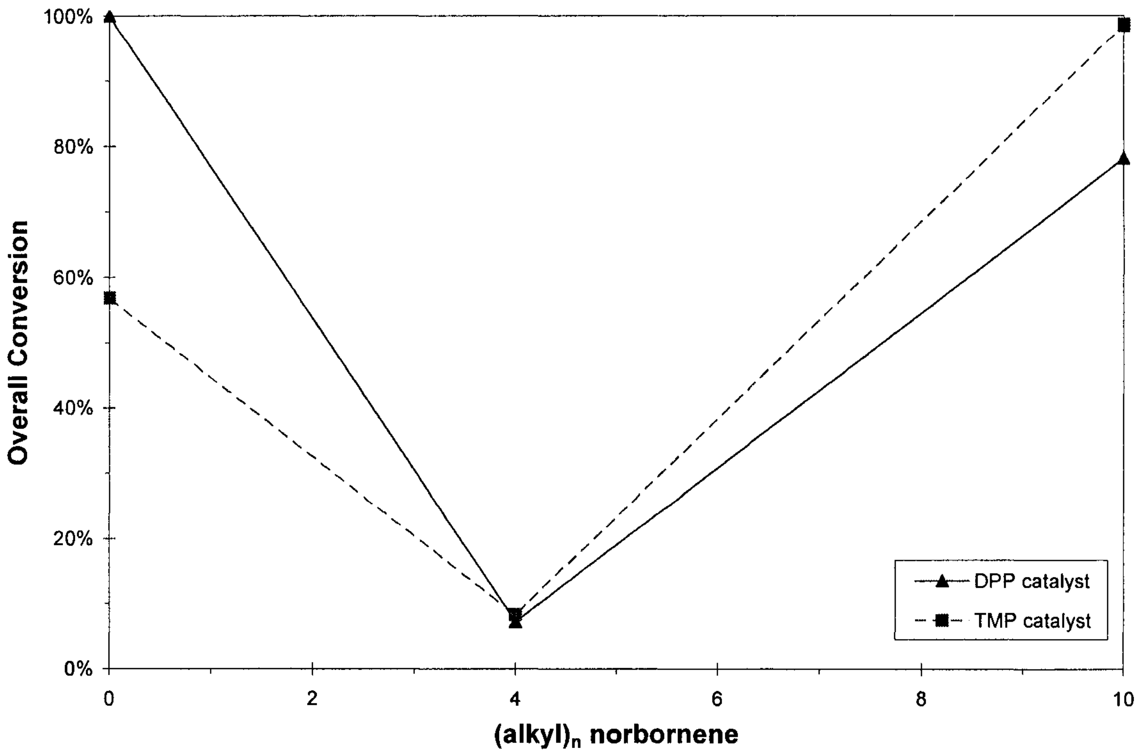


Figure 17. Overall norbornene conversion versus 5-alkyl-2-norbornene chain length in solution polymerization at 60°C with various catalysts.

NB-4 only reached low conversions (7-8%) with either catalyst, and those conversions were sensitive to the concentration of catalyst and activator. Raising the catalyst and activator concentrations by a factor of four increased the polymer conversion to 34 and 39% for the DPP and TMP catalysts, respectively. Even with this higher catalyst and activator concentration, the NB-4 conversion was still much lower than that for NB solution polymerization. A recent patent[33] describes the use of the TMP catalyst with LiFABA activator to polymerize NB-4 in toluene. With a catalyst concentration lower than the "standard" used in our studies (0.51 μmol/g NB compared to our 'standard' 1.34 μmol/g NB as shown in Table 1), the authors were able to achieve 91% conversion. Myagmarsuren et al.[32] and Funk et al.[49] found that NB-4 had a lower reactivity than NB due to the steric bulk of the butyl chain. Our results for NB-4 reactivity are significantly lower than that of Myagmarsuren and Funk, and also much less than the reactivity of NB. We will discuss more about the NB-4 conversion characteristics in the emulsion polymerization section of this paper.

NB-10 showed slight final conversion dependence with catalyst type, although reasonably high conversions were achieved with both catalysts. These solution polymerizations also showed a slight increase in viscosity during reaction, but polymer did not precipitate out of solution. This slight increase (rather than an expected large increase) in viscosity would seem to indicate that the poly (NB-10) might be of low molecular weight, but such measurements have not yet been made. Strangely, we did not observe clear glass transition temperatures (T_g) of the NB, NB-4, or NB-10 polymers, even upon heating to 400°C in the DSC. Overall, these solution polymerization results have shown that the allyl Pd catalyst – LiFABA activator pair has good activity for NB and NB-10 monomers and relatively much poorer activity for NB-4. The NB-10 shows a higher reactivity than expected, in contrast to Myagmarsuren[32] who found that as the alkyl chain length increased on the substituent, the monomer reactivity decreased.

Emulsion Polymerization

In this section of the paper we divide our discussions into those for the different classes of substituted norbornene monomers. As we do so, we note that in addition to the chemical structure differences between the monomers, there will also likely be differences in their water solubilities, something that is always important in emulsion polymerization. Indeed, as one looks at the various reaction pathways for norbornene catalytic emulsion polymerization with surfactant acting as a weakly coordinating anion, as shown in Figure 13, it is apparent that the production of latex particles via pathways 2 and 3 (but predominantly pathway 3) will gain or lose importance as the water solubility of the monomer is higher or lower, respectively. As we indicated previously[2], alkyl sulfate anions such as SDS interact favorably with the TMP catalyst to create small latex particles (via pathway 3) and establish a rate of polymerization that is quite competitive to that of the catalyst and LiFABA activator migrating to the emulsified droplets and producing large amounts of coagulum (agglomerates of ~10 μm polymer particles). Since norbornene has a water solubility of about that for styrene[13], adding substituents to the norbornene monomer at the 5 position is very likely to decrease their water solubility. Octanol to water partition coefficients for the monomers were predicted using 'property prediction software' from ChemSilico[50]. These results allowed us to rank the monomers by order of most to least water soluble. As such we have MeOH-NB > NB > Vinyl-NB > Butenyl-NB > NB-4 > NB-10.

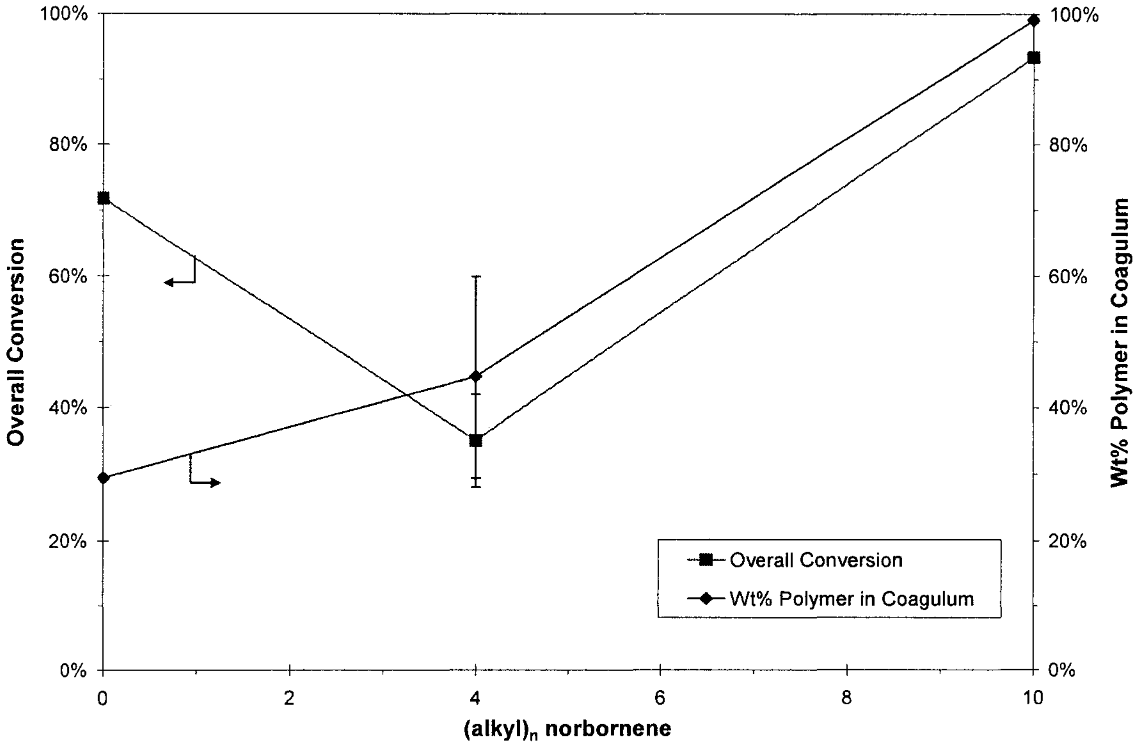
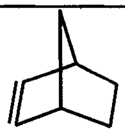
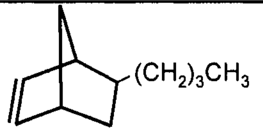
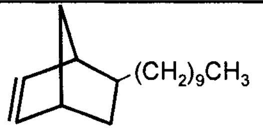
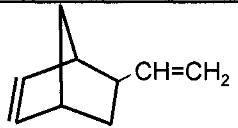
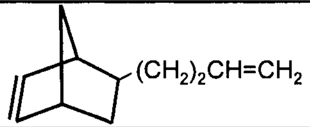
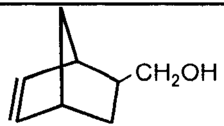


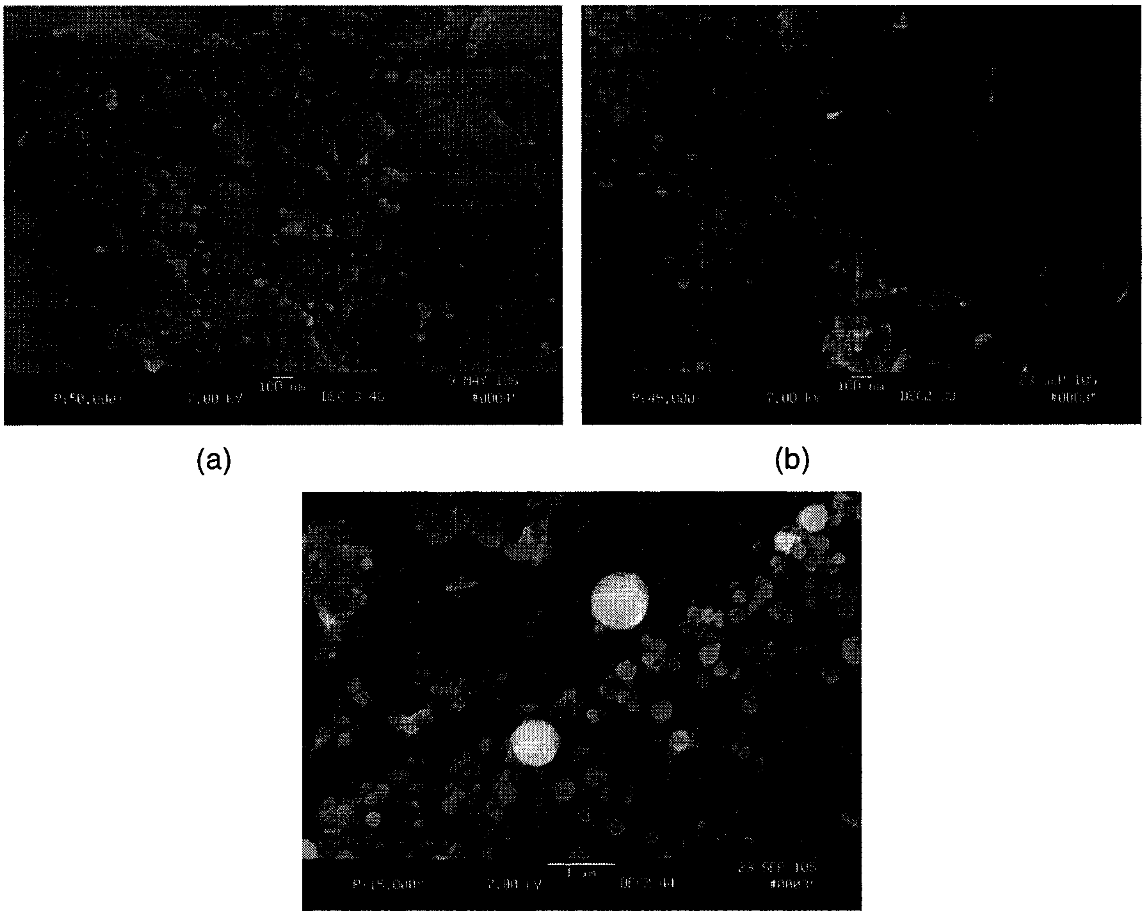
Figure 18. Overall conversion and amount of coagulum as a function of 5-alkyl-2-norbornene chain length in emulsion polymerization at 60°C with TMP catalyst and LiFABA activator.

The experimental results for the emulsion polymerization of the substituted norbornene monomers are displayed in Table 5. The results for the NB-4 and NB-10 are compared to those for norbornene itself in Figure 18 where we have plotted the overall monomer conversions and percent of polymer in coagulum form against the number of carbons in the substituted alkyl chain. When the final conversion (at the end of the 3 hour reaction) is less than 100%, we use the conversion level as an indication of the reactivity of the monomer with the catalyst and activator. As expected from the work of others with Pd catalyzed norbornene monomers[32,49], NB-4 is substantially less reactive than norbornene, in this case only achieving half the conversion of norbornene in the same reaction time. This is consistent with our solution polymerization results as discussed above, but the extent of the comparative decrease is much larger than that which others have reported in solution polymerization. Perhaps this is due to our particular catalyst system or an unusually high level of the *endo* isomer in the monomer. The latex particle sizes achieved were very nearly the same (45 nm via Nanotrac) for the two monomers and SEM photos are shown in Figure 19 (a) and (b).

The polymerization of NB-10 obtained nearly full conversion in the emulsion, consistent with that found in our solution polymerization experiment. These results are quite in contrast to those found by others[32,49] in that the apparent reactivity is higher than norbornene itself and very much greater than that for the butyl derivative. Given the likely water insolubility of the NB-10, is not surprising that there was only a very small portion of the polymer formed as latex particles. However, those that were formed were somewhat larger than those from NB and NB-4, as noted in the SEM photo in Figure 19 (c). What is perhaps the most distinctive about the data for the NB-10 is that nearly all of the polymer formed as coagulum. As noted in Figure 13, we believe that this would be due to the majority of reaction taking place along pathway 1. In fact, as we view all of the coagulum data in Table 5 and Figure 18 we see that the ratio of the amount of coagulum to latex particle polymer increases as the alkyl chain length becomes higher. We speculate that this is due to the relative water solubilities of the monomers, which should decrease substantially as one moves from NB to NB-4 to NB-10, and its impact on reducing the importance of reaction pathways 2 and 3. As these pathways are adversely affected by the water solubility of the monomers, pathway 1 is unaffected.

Table 5. Emulsion polymerization of various norbornene derived monomers using either TMP or DPP catalyst with LiFABA activator at 60°C

Experiment Number	wt% solids theoretical	wt% polymer in coagulum	% total conversion	Monomer		Catalyst
DEC2-37	5.7%	30%	71.8%	NB		TMP
DEC2-60	5.3%	50%	73.0%	NB		DPP
DEC2-85	5.1%	48%	69.9%	NB		DPP
DEC2-99	5.7%	31%	79.7%	NB		4x DPP
DEC3-20	5.4%	29%	82.8%	NB		4x DPP
DEC2-39	5.3%	56%	30.1%	NB-4		TMP
DEC2-81	5.0%	34%	39.9%	NB-4		TMP
DEC2-43	4.9%	44%	80.9%	NB-4		4x TMP
DEC3-44	5.1%	99%	93.4%	NB-10		TMP
DEC2-19	5.8%	89%	7.4%	Vinyl-NB		TMP
DEC2-20	5.4%	75%	9.6%	Vinyl-NB		TMP
DEC2-45	4.7%	22%	14.7%	Butenyl-NB		4x TMP
DEC2-41	5.2%	89%	48.8%	MeOH-NB		TMP



(a) (b)

(c)

Figure 19. SEM images of (a) NB, (b) NB-4, and (c) NB-10 latex particles produced in aqueous emulsion using TMP catalyst.

Returning to the unexpectedly low conversion levels achieved with the NB-4 in both solution and emulsion polymerizations, we determined the effect of increasing the TMP catalyst (and associated LiFABA) concentrations, while conducting the reactions at the same 60°C. Figure 20 shows these results and it is quite clear that major increases in reactivity were achieved in both systems. The response for norbornene in emulsion polymerization is also shown in Figure 20 for reference. Further, the data in Table 5 shows that the relative amounts of coagulum polymer to latex particle polymer were unchanged as the catalyst level was increased fourfold. It appears to us that the relative importance of the various reaction pathways shown in Figure 13 is unchanged as we add more catalyst and LiFABA activator. Since the SDS is present in great molar excess of the catalyst, its concentration did not have to be increased to allow pathway 3 to be impacted favorably by the increase in catalyst concentration. Alternatively, the LiFABA concentration had to be increased in the same proportion as the catalyst to have pathways 1 and 2 appropriately impacted. In this manner it is possible to understand why the conversion levels were higher but the fraction of polymer formed as coagulum remained constant. In addition we found that the particle size at the higher catalyst loading was 52 nm (via Nanotrac) and shown as SEM photos in Figure 21 (a) and (b).

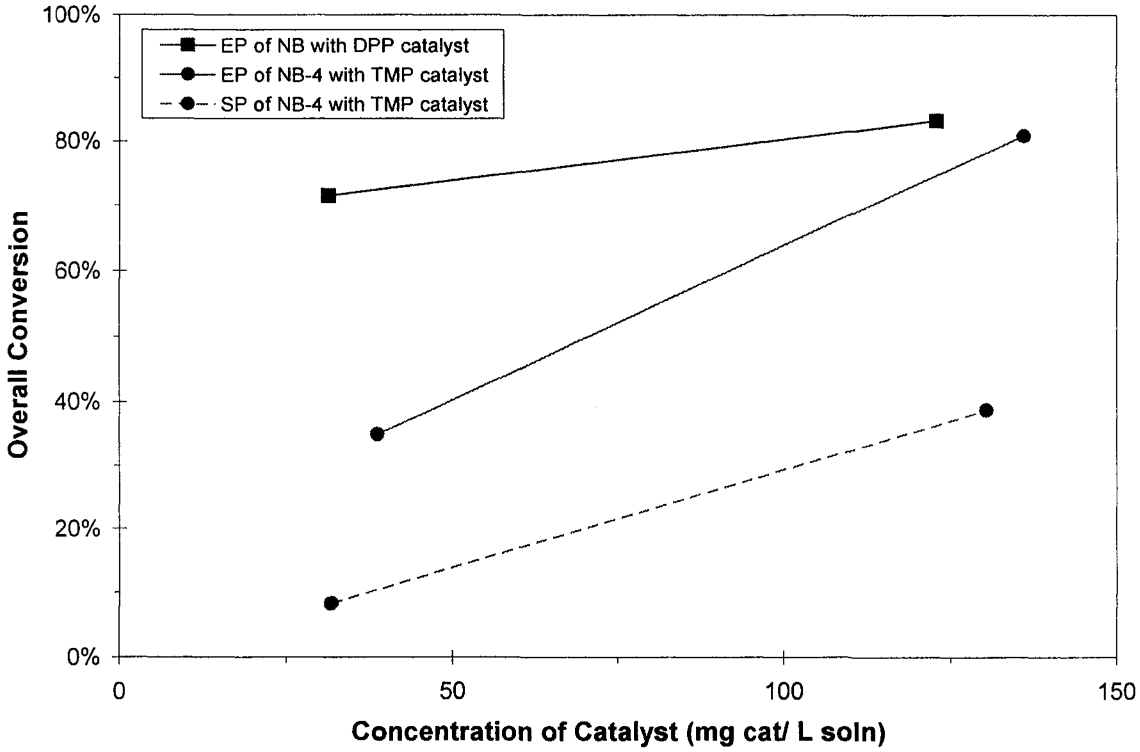
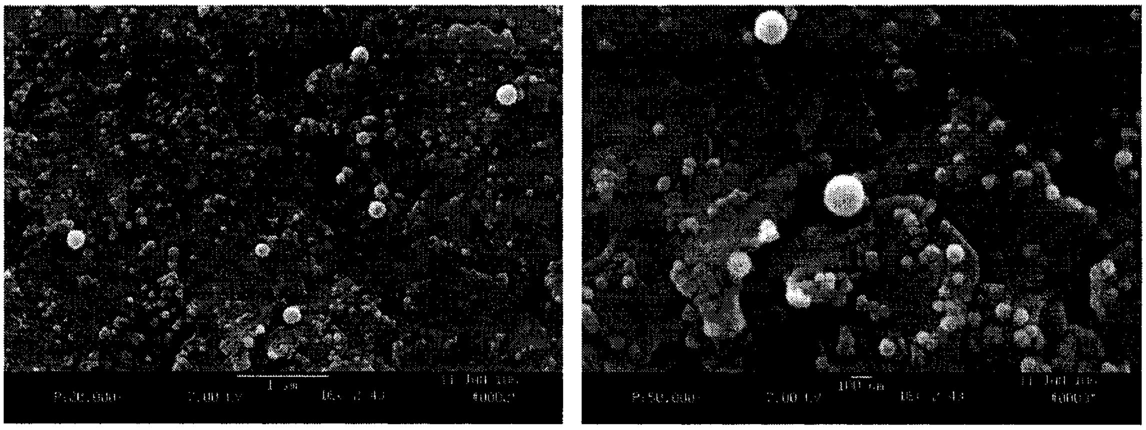


Figure 20. Overall conversion of NB and NB-4 in emulsion (EP) or solution (SP) as a function of either TMP or DPP catalyst concentration.



(a) (b)

Figure 21. SEM images of P(NB-4) latex particles produced at 4x the standard TMP catalyst concentration.

We were interested in experimenting with vinyl substituted norbornenes as a means to obtain NB type latices that contained pendant vinyl groups on the polymer chains. One can imagine that these latex particles might serve as seed particles for the creation of composite latex particles (perhaps with acrylics) and that the pendant double bonds might lead to the ability to form graft copolymers using free radical initiators. When we reacted these monomers in emulsion polymerization (we did not perform comparative studies in solution), we found that the conversion level achieved for the vinyl NB was only 8-9 % in the 3 hour reaction time. It seems the water solubility of this monomer should not be greatly lower than that for NB and thus that the suppression of the reactivity was likely due to the *endo* isomer retarding the polymerization rate. For the butenyl-NB, we increased the catalyst and activator concentrations by a factor of four in order to achieve high conversion, but only achieved 15%. Given the discussion in the literature about the suppression of reaction rates by the substituent groups on the NB ring, we had thought that the butenyl derivative might not retard the rate as much as the vinyl derivative due to the possibility of chelation via a six-membered ring in the latter and not in the former. At this point we cannot offer any further analysis of the results for these two monomers.

A last new monomer experiment was conducted with methanol NB in an attempt to change the polar nature of the substituted group. Oxygen containing side groups on the NB (e.g. carboxylic acid) are known to seriously degrade the reactivity of the monomer in solution polymerization[48,49], and thus we expected a retardation in our emulsion polymerization rate with this monomer. Table 5 shows that we only achieved 48% conversion with this monomer. Puech et al.[40] polymerized MeOH-NB to 80% conversion using $PdCl_2(TPPTS)_2$ catalyst in water over a reaction time of 24 hours. Perhaps an extension of our reaction time would have improved the conversion level. In contrast to some of the other monomers described in this paper, the 48% conversion figure is not nearly as poor as some of the others, being about two-thirds as active as norbornene. However, the vast majority of the polymer was produced as coagulum. This result is not consistent with the idea that the water solubility might be slightly higher than norbornene and that we might expect similar retardation effects on the reactivity characteristics in both the water environment (reaction pathways 2 and 3) and the bulk monomer environment (pathway 1). This remains unexplained.

Mini-Emulsion of Decyl-norbornene

As we showed above, the very hydrophobic monomer, NB-10, could be polymerized to a high extent with catalyst and activator in aqueous emulsion, however 99% of the polymer was formed as coagulum. To show that the polymer particles could be stabilized by SDS if they were smaller, NB-10 was mini-emulsified with SDS to produce 120 nm droplets of monomer, and then catalyst and activator were added to the reactor. The resulting particles were all stable latex particles with a diameter of 190 nm, as seen in the particle size distribution curves in Figure 22. We did not add any compound to prevent Ostwald ripening so we might have experienced some particle size increase by this mechanism. The sonified NB-10 resulted in 96% conversion with none of the polymer as coagulum. The catalyst and activator were apparently able to migrate to the monomer droplets to effect polymerization in that location. New particles were not nucleated during this experiment, which shows that we had a 'true' mini-emulsion where the polymerization occurred in the monomer droplets. These results complement those noted earlier – the catalyst and activator easily migrate through the water to penetrate small (mini-emulsified) or larger (normally emulsified) monomer droplets and promote reaction within them. The SDS appears to stabilize the 190 nm particles while it does not stabilize micron sized polymer particles.

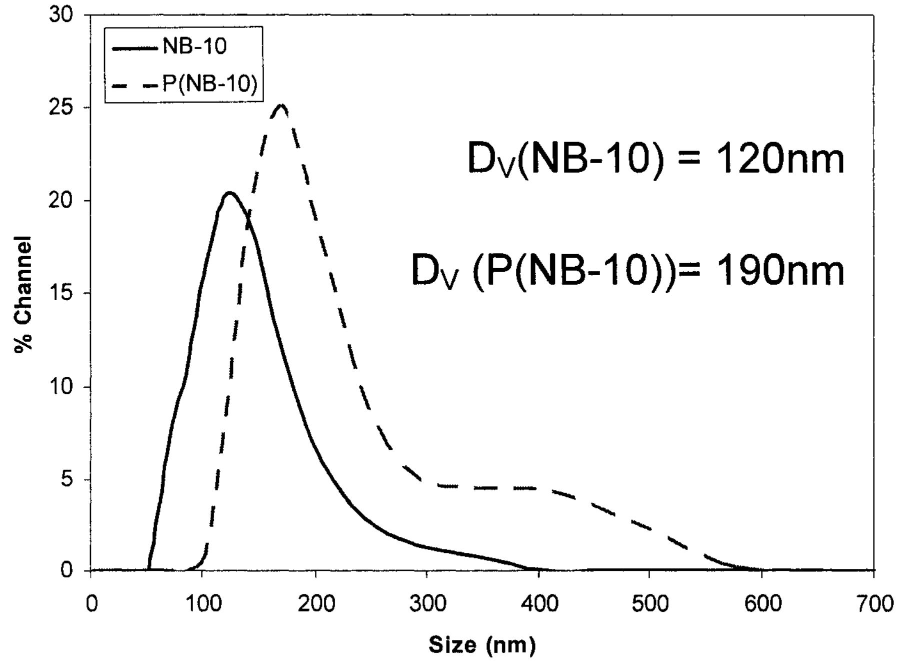


Figure 22. Nanotrac particle size results of sonified NB-10 monomer and the resulting P(NB-10) latex.

Concluding Remarks

It is quite evident that substituted norbornene monomers have lower reaction rates than the parent norbornene, as shown previously by others in solution polymerization. Our results have further demonstrated that this is also true in emulsion polymerization when using a consistent Pd based catalyst and activator system as one moves from solution to emulsion polymerization systems. In contrast to other studies, our results do not show a continual decrease in the reactivity of n-alkyl substituted norbornenes over the range of 0-10 carbons in the chain. The reactivities of these alkyl norbornenes are affected by the catalyst concentration in both solution and emulsion systems, as might be expected. We find that the apparent mechanisms for latex particle formation for these substituted norbornene monomers is the same as that for norbornene, and that large amounts of coagulum can be formed when the catalyst and activator are allowed to migrate to the emulsified monomer droplets and effect polymerization in that location. Such large polymer particles are not stabilized by SDS. Alternatively the very non-polar decyl-norbornene can be polymerized to form a colloidally stable latex at ca. 200 nm particle size with the same level of SDS by using the mini-emulsion polymerization process.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The work in this thesis, as well as previous works[4-13,26-38], has shown that palladium-based catalysts can polymerize norbornene via a vinyl polymerization mechanism in organic solutions. The polymerization mechanism in solution appears to be simpler than in emulsion. In water, there is a competition between the organic and aqueous phase polymerization sites for the reaction of norbornene. As a contrast, in standard free radical emulsion polymerization, reaction in the large emulsified monomer droplets is not important relative to the much faster reactions in the aqueous/micellar environment. However, in the catalytic emulsion polymerization of norbornene via allyl Pd-based catalysts, that appears to not be the case. In an aqueous environment, without surfactant, the catalyst and activator migrate through the water phase into the emulsified norbornene droplets where they promote polymerization. The catalyst appears to retain its activity as it migrates through the water phase, and is still active to promote polymerization in the monomer droplets. This reaction pathway produces unstable latex particles that coagulate mainly due to their size (~10 μm). A secondary reaction pathway also exists in the water phase with the catalyst and activator, which produces small stable latex particles (ca. 50 nm). This is a relatively slow reaction and hardly competes with the emulsified droplet polymerization.

The addition of surfactant to aqueous emulsion with catalyst and activator can provide a new and effective pathway toward stable latex particles. The efficacy of forming stable latex particles is determined by the surfactant's ability to activate the catalyst. Various classes of surfactants were examined and it was found that the alkyl sulfates and sulfonates effectively activate the palladium catalyst and that the alkyl chain length affects the activation capabilities of the catalyst. Other surfactants destructively interfere with the either catalyst or the activator and prevent polymerization (e.g. the cationic surfactant destructively interfered with the FABA anion preventing polymerization in the monomer droplets or the water phase). The sulfate and sulfonate surfactants can act as weakly coordinating anions in the aqueous phase to activate the catalyst, and thus replace the need for the traditional activators, such as LiFABA. Infact, sodium hexadecyl sulfate can produce stable latices with very little coagulum formation by effectively competing with the catalyst and activator in the monomer droplet. The role of the surfactant in activating the catalyst in norbornene emulsion polymerization sets it in striking contrast to the traditional role of the surfactant in standard free radical emulsion polymerization where the surfactant can serve to nucleate and then stabilize the latex particles, but it does not influence the inherent activity of the initiator.

Finally, it has been shown that substituted norbornene monomers have lower reaction rates than the parent norbornene. This has been previously shown by others in solution polymerization[32,48,49]. This work has further demonstrated that this is also true in emulsion polymerization when using an allyl Pd-based catalyst and activator system. In contrast to other studies, the present work does not show a continual decrease in the reactivity of n-alkyl substituted norbornenes over the range of 0-10 carbons in the chain. The apparent mechanisms for latex particle formation for these substituted norbornene monomers is the same as that for norbornene, and large amounts of coagulum can be formed when the catalyst and activator are allowed to migrate to the emulsified monomer droplets and effect polymerization in that location. Alternatively, the very non-polar 5-decyl-2-norbornene can be polymerized to form a colloidally stable latex at ca. 200 nm particle size with the same level of SDS by using the mini-emulsion polymerization process.

Recommendations

There are still many unanswered questions about the mechanism of polymerization of norbornene in an aqueous environment. Questions about molecular weight development, copolymerization with other olefins, heat of reaction, and the possibility of creating composite particles have not yet been examined.

It has been proposed that the polymerization is a living polymerization, with one catalyst center used for each polymer chain. Thus, we might expect that with an increase in catalyst concentration the molecular weight would decrease. But after several experiments of this kind, the resulting polymer was still not soluble in solvents tried, thus leaving us without molecular weight data. A study should be performed where polymers with low molecular weights are formed and their chain lengths measured (i.e., via GPC). Such a study relating catalyst concentration to molecular weight would also aid in more fully understanding the polymerization mechanisms. This should be done in both solution and emulsion as there appears to be differences in polymerization mechanisms.

The ultimate goal of this project was to understand the mechanism of norbornene polymerization in emulsion and apply that knowledge to the copolymerization of ethylene and norbornene. It would be interesting to extend that study to the copolymerization of norbornene and other norbornene derivatives and α-olefins as well as to develop an understanding of the mechanism of copolymerization.

A ‘heat kick’ was not observed during any of the norbornene polymerizations, which is surprising because the majority of the reaction occurred within 60 minutes of the catalyst and activator being added to the reactor. In standard free radical polymerizations, the heat of polymerization is quite large, and once at an industrial scale, heat transfer needs to be carefully taken into consideration for reactor temperature control. Thus, it would be of interest to determine the heat of polymerization of polynorbornene. This may be best accomplished in solution polymerization using a reaction calorimeter.

Polynorbornene in latex form may not be an interesting polymer alone because of its high glass transition temperature, but it may be of interest if used as the basis for a composite polymer. If copolymerization of various norbornene monomers can be made via catalytic emulsion polymerization, these copolymers could be used as a seed latex. An acrylic second stage could then be polymerized via free radical emulsion polymerization, using the polynorbornene latex as a seed latex. This composite polymer may yield novel mechanical properties or provide cost advantages. This avenue of polynorbornene seed latex and acrylic second stage should be pursued.

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APPENDICES

APPENDIX A

Catalytic Emulsion Polymerization of Norbornene – DPP catalyst

The majority of the experiments were performed in aqueous emulsion using the standard recipe noted below. The standard polynorbornene reaction is shown in Table 1. This recipe is 5% polymer latex solids, which in the table is noted 'PNB latex.' The table lists the experimental number, the theoretical weight percentage of solids (typically around 5%), the measured latex solids, the latex conversion (determined from the measured latex solids and the theoretical solids), the weight percent of polymer that is in coagulum form, and the total conversion (determined from the total polymer formed from latex and coagulum from the theoretical polymer that could be formed). The 'Comments' column indicates the difference between the standard PNB latex. For example, DEC2-79 has a comment 'PNB latex w/SHDS' which indicates that rather than the standard SDS surfactant, SHDS (sodium hexadecyl sulfate) was used in the polynorbornene reaction. DEC3-39a has a comment 'PNB latex w/o activator' indicating that the standard PNB latex recipe applies, but the activator is completely omitted. Appendix A is specific to reactions using the DPP catalyst, while Appendix B is specific to reactions using the TMP catalyst.

Table 1. Standard polynorbornene polymerization recipes

Polymerization Recipes

	Emulsion		Solution	
DI Water	95	g	----	
Cylcohexane	----		95	g
Monomer	5	g	5	g
Acetone	0.5	g	0.5	g
SDS	0.25	g	----	
Catalyst	3.2	mg	3.2	mg
Activator	5.6	mg	5.6	mg
THF	1	g	1	g
Temperature	60	°C	60	°C

Experiment Number	wt% solids theoretical	wt% solids measured	wt% polymer in coagulum form	% conversion in latex	% total conversion	Comments
DEC2-38	5.68%	2.13%	57.6%	37.6%	88.6%	PNB latex
DEC2-50	4.84%	2.31%	34.7%	47.8%	73.3%	PNB latex
DEC2-51	5.04%	2.28%	46.3%	45.2%	84.2%	PNB w/ cat/act added after NB
DEC2-52	4.64%	0.41%	79.1%	8.8%	41.9%	P(NB-4) latex
DEC2-54	4.51%	0.37%	80.7%	8.2%	42.7%	P(NB-4) latex
DEC2-55	5.06%	0.00%	0.0%	0.0%	0.0%	PNB latex w/ Sodium Stearate
DEC2-57	5.00%	0.00%	0.0%	0.0%	0.0%	PNB latex w/ Sodium Stearate + TSPP
DEC2-59	5.33%	2.03%	36.0%	38.0%	59.5%	PNB latex w/ Rhodapex CO-436
DEC2-60	5.26%	1.93%	49.8%	36.6%	73.0%	PNB latex w/SDS
DEC2-61	5.08%	1.65%	48.6%	32.6%	63.4%	PNB latex w/RDP and SDS
DEC2-62	5.03%	0.14%	83.4%	2.7%	16.3%	PNB latex w/DBSA
DEC2-63	5.33%	1.25%	33.4%	23.4%	35.1%	PNB latex w/Aerosol OT
DEC2-64	4.78%	2.51%	33.9%	52.4%	79.4%	PNB latex w/ STDS
DEC2-65	5.28%	1.55%	55.5%	29.2%	65.7%	PNB latex w/ SODS
DEC2-66	5.62%	2.41%	33.2%	42.8%	64.1%	PNB latex w/ Na hexadecane SO3
DEC2-67	5.31%	3.51%	23.7%	66.1%	86.7%	PNB latex w/ STDS
DEC2-68	4.96%	2.41%	30.8%	48.5%	70.1%	PNB latex w/ SODS
DEC2-69	5.44%	0.77%	80.9%	14.1%	74.0%	PNB latex w/ SDecS
DEC2-70	4.70%	0.27%	92.4%	5.8%	76.0%	PNB latex w/o surfactant
DEC2-71	4.73%	1.41%	34.7%	29.9%	45.8%	PNB latex w/SDS reacts for 15min
DEC2-72	5.16%	1.98%	38.1%	38.3%	61.8%	PNB latex w/SDS reacts for 1 hour
DEC2-73	5.47%	0.61%	80.9%	11.1%	57.9%	PNB latex w/ non-ionic 5 EO chains
DEC2-74	4.73%	0.22%	4.6%	4.6%	11.1%	PNB latex w/ non-ionic 100 EO chains
DEC2-75	4.56%	0.63%	54.5%	13.8%	30.2%	PNB latex w/ non-ionic 5 EO w/SDS
DEC2-76	4.85%	0.40%	81.2%	8.2%	43.9%	PNB latex w/ non-ionic 100 EO w/SDS
DEC2-77	5.30%	2.99%	35.6%	56.5%	87.6%	PNB latex w/ 0.02M NaCl
DEC2-78	5.83%	4.04%	22.3%	69.3%	89.2%	PNB latex w/ 2x STDS
DEC2-79	4.95%	3.52%	10.9%	71.2%	79.9%	PNB latex w/ SHDS
DEC2-80	4.74%	0.07%	30.6%	1.4%	2.0%	PNB latex w/ CTAB
DEC2-82	5.21%	3.87%	8.3%	74.4%	81.1%	PNB latex w/ SHDS
DEC2-83	5.36%	1.95%	49.8%	36.5%	72.6%	PNB latex w/ SDS reacts for 22 hours
DEC2-84	9.07%	5.68%	21.8%	62.6%	80.0%	10% PNB latex w/ SHDS
DEC2-85	5.13%	1.86%	48.0%	36.3%	69.9%	PNB latex w/SDS reacts for 3 hours
DEC2-86	6.18%	1.89%	58.2%	30.5%	73.1%	PNB latex w/ 0.06M NaCl
DEC2-87	4.92%	0.91%	51.5%	18.5%	38.2%	PNB latex w/ 0.17M NaCl
DEC2-88	4.81%	1.40%	59.0%	29.0%	70.9%	PNB latex w/ 4x [cat/act]
DEC2-90	5.18%	3.02%	12.1%	58.3%	66.3%	PNB w/ 2x SHDS
DEC2-91	5.12%	2.72%	36.8%	53.1%	84.0%	PNB latex w/ 0.02M NaCl
DEC2-92	5.04%	2.24%	33.8%	44.4%	67.2%	PNB latex w/o thorough O2 purging
DEC2-94	5.45%	3.40%	28.4%	62.5%	87.3%	PNB latex w/ 4x [cat/act]
DEC2-96	4.98%	2.64%	24.3%	53.0%	70.1%	PNB latex w/o thorough O2 purging
DEC2-98	4.97%	2.47%	26.5%	49.7%	67.6%	PNB w/ 0.02M NaHCO3
DEC2-99	5.70%	3.15%	30.6%	55.3%	79.7%	PNB w/ 4x [cat/act]
DEC3-03	4.98%	2.10%	38.7%	37.3%	60.9%	PNB Trxn = 70C
DEC3-04	5.71%	2.00%	52.3%	30.6%	64.2%	PNB Trxn = 70C (stirring stopped)
DEC3-05	5.77%	0.97%	81.3%	12.3%	65.7%	PNB Trxn = 80C
DEC3-06	5.95%	0.50%	93.6%	3.6%	56.3%	PNB Trxn = 80C
DEC3-07	4.97%	2.81%	28.9%	51.7%	72.7%	PNB Trxn = 50C
DEC3-08	5.63%	3.53%	30.5%	57.9%	83.3%	PNB Trxn = 50C
DEC3-10	8.92%	5.19%	29.6%	54.8%	77.9%	10% PNB fed w/ SHDS
DEC3-12	5.93%	2.90%	14.9%	40.1%	56.6%	P(NB-St) with cat and KPS initiator
DEC3-13	5.06%	4.25%	7.1%	83.9%	90.3%	PNB latex w/ 2x STDS
DEC3-14	5.26%	0.56%	30.4%	10.7%	15.4%	PNB latex w/ non-ionic 40 EO

Experiment Number	wt% solids theoretical	wt% solids measured	wt% polymer in coagulum form	% conversion in latex	% total conversion	Comments
DEC3-15	5.02%	1.09%	18.7%	21.7%	26.7%	PNB latex w/ non-ionic 40 EO w/SDS
DEC3-17	11.64%	3.05%	62.4%	13.8%	51.1%	P(St-BuA)seed PNB 2nd stage
DEC3-18	5.42%	0.43%	22.6%	7.9%	10.1%	PNB latex w/ non-ionic 12 EO
DEC3-19	4.73%	1.29%	57.9%	27.3%	64.8%	PNB latex w/ 1/3 [cat]
DEC3-20	5.41%	3.16%	29.4%	58.4%	82.8%	PNB latex w/ 4x [cat]
DEC3-32	5.19%	1.41%	67.7%	27.1%	83.7%	PNB latex w/ 10x [cat]
DEC3-35	5.45%	3.60%	13.2%	65.0%	78.8%	PNB seeded from PS grown to 100nm
DEC3-37	5.29%	2.82%	26.6%	53.1%	73.5%	PNB seeded from PS grown to 200nm
DEC3-39 a	5.11%	1.83%	35.4%	35.8%	55.5%	PNB latex w/o activator
DEC3-43	5.00%	0.00%	0.0%	0.0%	0.0%	PNB-10 in emulsion w/ Strem cat
DEC4-11	4.63%	2.79%	26.9%	60.2%	82.4%	PNB latex w/ 4x [act]
DEC4-12	5.15%	2.68%	38.5%	52.0%	84.6%	PNB latex w/ 10x [cat/act]
DEC4-14	5.00%	2.75%	31.6%	55.1%	80.5%	PNB latex w/ 2x [cat] 8x[act]
DEC4-15	5.32%	2.94%	29.2%	55.4%	78.2%	PNB latex w/ 10x [act]
DEC4-19	5.51%	3.66%	3.4%	66.4%	68.7%	PNB latex w/o activator

APPENDIX B

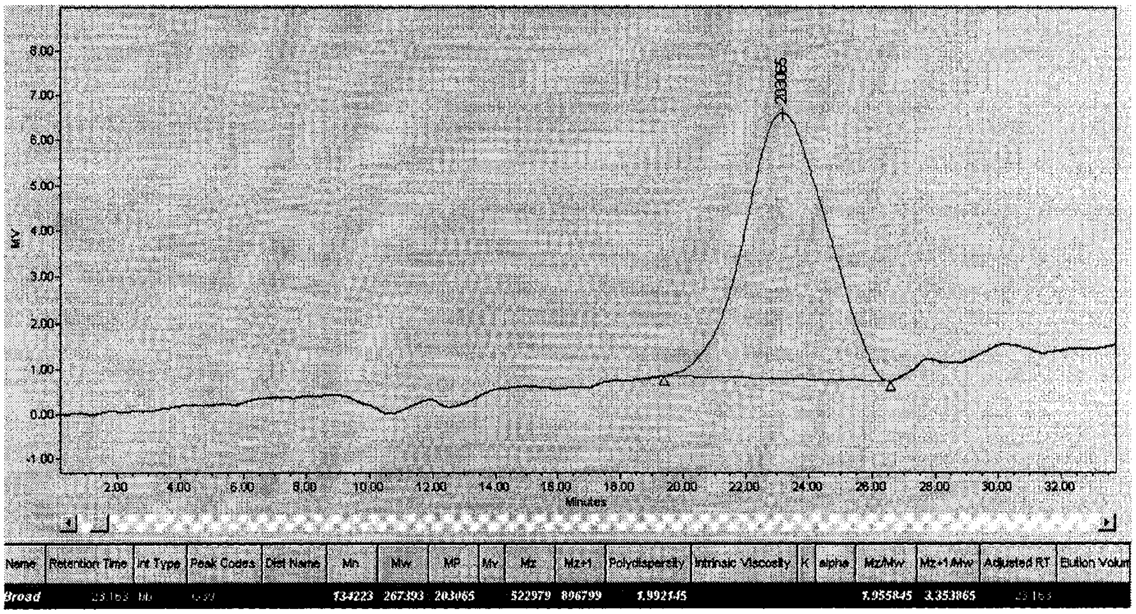
Catalytic Emulsion Polymerization of Norbornene – TMP catalyst

Experiment Number	wt% solids theoretical	wt% solids measured	wt% polymer in coagulum form	% conversion in latex	% total conversion	Comments
DEC2-02	10.14%	3.24%	27.8%	20.3%	28.1%	feeding NB/acetone mix 5 hrs
DEC2-03	5.53%	2.27%	39.7%	25.7%	42.5%	feeding NB/acetone mix 5 hrs
DEC2-04	5.19%	2.05%	39.9%	20.4%	33.8%	repeat -syringe clogged conv est
DEC2-05	5.01%	2.74%	28.0%	35.4%	49.1%	1% initial solids - feeding 1.5hrs
DEC2-06	4.61%	2.42%	33.2%	47.1%	70.5%	0.5% initial solids - feeding 1.5hrs
DEC2-07	8.73%	4.40%	18.0%	47.7%	58.1%	0.5% initial solids - feeding 1.5hrs
DEC2-08	6.19%	1.69%	24.1%	24.4%	32.1%	PNB seed used in Batch growth of PNB
DEC2-09	6.13%	2.93%	203.5%	45.2%	64.5%	0.5% PNB seed starve fed
DEC2-10	6.01%	1.49%	56.7%	24.4%	56.4%	5% PNB solids Batch
DEC2-11	5.00%	0.62%	73.0%	9.7%	36.0%	Starve-fed NB (no PNB at beginning)
DEC2-12	8.65%	3.48%	30.7%	40.3%	63.7%	P(St-BA) seed grown w/NB (500% SR)
DEC2-13	5.81%	0.97%	57.9%	15.6%	37.1%	0.5% initial solids - feeding 1.5hrs - DBSA
DEC2-17	5.00%	0.00%	0.0%	0.0%	0.0%	vinyl-NB w/KPS initiator
DEC2-18	5.00%	0.00%	0.0%	0.0%	0.0%	vinyl-NB w/KPS initiator
DEC2-19	5.00%	0.00%	0.0%	0.0%	0.0%	vinyl-NB w/ cat/act and KPS init
DEC2-20	5.00%	0.00%	0.0%	0.0%	0.0%	vinyl-NB w/ cat/act and KPS init
DEC2-21	14.75%	3.12%	163.0%	7.3%	15.2%	P(MMA-MA) seed PNB 2nd stage-Batch
DEC2-22	8.96%	6.93%	42.8%	74.7%	77.3%	PNB seed PMA 2nd stage-Batch
DEC2-23	5.45%	0.67%	219.5%	0.1%	44.0%	P(NB/Vinyl-NB) 50/50 mixture-Batch
DEC2-24	10.30%	4.72%	44.1%	18.9%	55.7%	P(St-BA) seed grown w/NB (200% SR)
DEC2-25	9.54%	3.35%	23.9%	32.3%	42.5%	0.5% initial solids - feeding 1.5hrs
DEC2-27	4.83%	2.77%	20.7%	57.4%	72.3%	5% PNB solids Batch 0.2wt% octene
DEC2-29 -1	4.85%	1.21%	82.9%	25.0%	58.2%	PNB Batch at R&H
DEC2-29 -3	4.85%	0.83%	80.7%	17.1%	89.0%	P(4-NB) Batch at R&H
DEC2-31	9.88%	1.49%	7.5%	15.1%	15.5%	10% PNB solids starve-fed seed at R&H
DEC2-33	5.9%	5.30%	-217.3%	87.3%	65.6%	PNB seed P(St-BuA) 2nd stage at R&H
DEC2-34	4.89%	1.07%	0.0%	21.8%	21.8%	PNB-4 at room temp at R&H
DEC2-37	5.73%	2.90%	29.5%	50.6%	71.8%	PNB latex
DEC2-39	5.32%	0.71%	55.5%	13.4%	30.1%	PNB-4 latex
DEC2-41	5.24%	0.29%	88.5%	5.6%	48.8%	P(MeOH-NB) latex
DEC2-42	5.63%	2.95%	14.8%	52.4%	61.5%	PNB add cat/act before NB
DEC2-43	4.90%	2.21%	44.2%	45.1%	80.9%	PNB-4 w/ 2x [cat/act]
DEC2-44	4.68%	1.18%	69.9%	25.2%	83.7%	PNB-4 latex
DEC2-45	4.72%	0.54%	22.1%	11.5%	14.7%	P(butenyl-NB) [cat/act]
DEC2-46	5.50%	2.95%	38.2%	53.6%	60.4%	PNB add cat/act before NB
DEC2-47	4.90%	0.86%	62.5%	17.5%	46.6%	P(MeOH-NB/NB) latex
DEC2-48	4.97%	0.44%	29.5%	9.0%	12.7%	P(butenyl-NB/NB) latex
DEC2-49	4.82%	1.79%	52.7%	37.2%	78.6%	P(NB-4/NB) latex
DEC2-53	4.72%	1.89%	43.2%	35.1%	61.7%	PNB feed
DEC2-58	20.48%	19.61%	0.0%	95.7%	95.7%	PS latex w/ Sodium Stearate
DEC2-81	4.95%	1.31%	33.9%	26.4%	39.9%	PNB-4 latex
DEC2-89	5.29%	3.26%	12.4%	61.7%	70.4%	PNB w/ SHDS
DEC2-93	5.75%	3.57%	20.7%	62.1%	78.3%	PNB w/ SHDS
DEC2-95	5.09%	2.39%	30.6%	46.9%	67.5%	PNB latex w/o thorough O2 purging
DEC2-97	4.93%	1.79%	45.8%	36.4%	67.1%	PNB latex w/o thorough O2 purging
DEC2-100	5.10%	2.49%	29.6%	48.9%	69.4%	PNB w/ 0.02M IS
DEC3-01	5.54%	3.18%	29.0%	57.4%	80.9%	PNB w/ 0.02M IS w/ SHDS
DEC3-11	6.23%	0.71%	81.4%	11.4%	61.2%	P(MeOH-NB) w/ 4x [cat/act]
DEC3-33	5.63%	3.34%	25.7%	59.4%	80.0%	PNB latex
DEC3-34	5.37%	2.02%	57.5%	37.6%	88.6%	PNB latex w/ 10x [cat/act]
DEC3-36	5.83%	2.62%	28.0%	43.4%	69.1%	PS seed PNB 2nd stage (target = 100nm)
DEC3-38	5.52%	2.74%	30.7%	49.6%	73.5%	PS seed PNB 2nd stage (target = 200nm)
DEC3-39 b	5.25%	3.32%	3.6%	63.4%	65.7%	PNB latex w/o activator

Experiment Number	wt% solids theoretical	wt% solids measured	wt% polymer in coagulum form	% conversion in latex	% total conversion	Comments
DEC3-41	5.64%	1.09%	22.9%	19.2%	25.0%	PNB latex w/o activator Trxn = 80C
DEC3-42	5.30%	2.98%	28.9%	50.9%	71.5%	PNB latex w/SHDS - fed NB
DEC3-44	5.11%	0.04%	99.1%	0.9%	93.4%	PNB-10 in emulsion w/cat/act
DEC3-46	5.13%	3.19%	5.4%	62.3%	65.8%	PNB latex w/o activator
DEC3-47	5.48%	3.11%	7.4%	56.8%	61.4%	PNB latex w/o activator w/SHDS
DEC3-48	18.70%	1.38%	1.0%	7.4%	7.5%	20% PNB latex w/o act
DEC3-49	9.78%	3.02%	2.3%	30.8%	31.6%	10% PNB latex w/o act
DEC3-50	11.41%	2.40%	67.6%	21.0%	64.7%	10% PNB latex w/ 1hr late add of act
DEC3-51	11.83%	2.96%	48.9%	25.0%	48.9%	10% PNB latex w/ 2hr late add of act
DEC3-53	3.07%	1.99%	6.8%	64.7%	69.4%	3% PNB latex w/o act
DEC3-54	5.06%	0.05%	75.5%	0.9%	3.8%	PNB-10 latex w/o act
DEC3-55	9.62%	2.39%	1.1%	24.8%	25.1%	10% PNB latex w/o act w/ 2x [SDS]
DEC3-56	10.61%	3.95%	0.8%	37.2%	37.5%	10% PNB latex w/o act w/ 2x [cat]
DEC3-57	5.57%	2.07%	54.0%	24.3%	69.4%	PS seed PNB 2nd stage
DEC3-58	5.15%	1.26%	50.9%	24.4%	59.7%	P(St-BuA) seed PNB 2nd stage
DEC3-59	9.24%	1.33%	59.4%	14.4%	50.1%	Repeat DEC2-12 (P(St-BuA) PNB)
DEC3-61	9.50%	0.00%	0.0%	0.0%	0.0%	10% PNB latex w/ 36x [SDS] w/activator
DEC3-62	9.83%	1.34%	2.3%	13.6%	13.9%	10% PNB latex w/o act trxn ~ 24hrs
DEC3-63	5.80%	2.97%	25.5%	51.2%	68.7%	5% PNB w/o act - Added act (after 3hrs)
DEC3-64	9.58%	4.02%	31.3%	41.9%	50.6%	PNB w/o act - Added act after 3hrs and fed NB
DEC3-65	7.73%	3.26%	17.6%	42.2%	51.2%	1% PNB w/o act - Added act and fed to 8% solids
DEC3-66	5.81%	1.84%	0.7%	47.7%	48.3%	2% PS seed (25nm) to 6% PNB 2nd stage w/o act
DEC3-67	5.77%	1.92%	2.7%	48.3%	50.3%	2% PS seed (55nm) to 6% PNB 2nd stage w/o act
DEC3-68	8.49%	2.69%	6.3%	31.6%	34.9%	4% PS seed (25nm) to 12% PNB 2nd stage w/o act
DEC3-69	9.18%	2.74%	6.2%	29.8%	32.7%	4% PS seed (55nm) to 12% PNB 2nd stage w/o act
DEC3-70	4.17%	0.83%	45.4%	19.9%	58.6%	PS seed PNB 2nd stage w/ cat/act
DEC3-71	7.51%	2.35%	34.3%	31.2%	66.5%	PS seed swollen w/NB and act - added cat
DEC3-72	11.53%	2.93%	3.4%	25.5%	26.4%	10% PNB with 2 shots of cat and NB w/o act
DEC3-74	5.19%	3.67%	2.9%	70.9%	73.0%	5% PNB with 2 shots of cat w/o act
DEC3-75	4.21%	1.76%	6.6%	41.8%	66.3%	PS seed swollen w/NB and act
DEC3-76	9.79%	4.55%	5.6%	46.4%	49.2%	PNB (5% w/o act - shot SDS.NB, & cat to 10%)
DEC3-77	5.23%	1.91%	3.3%	36.5%	37.7%	5% PNB latex with AgPF6
DEC3-78	5.44%	0.00%	--------	---------	0.0%	soln polym NB in cylcohexane
DEC3-79	5.11%	2.04%	2.4%	39.9%	40.9%	5% PNB latex with AgPF6
DEC3-80	5.33%	0.34%	0.0%	6.4%	6.4%	5% PNB latex with AgPF6
DEC3-81	9.20%	4.75%	1.8%	51.6%	52.5%	10% PNB w/ 2x [SHDS] w/o act
DEC3-82	9.69%	3.68%	2.8%	38.0%	39.1%	10% PNB w/ 3x [SDS] w/o act
DEC3-84	5.75%	1.57%	2.6%	27.3%	28.1%	5% PNB latex with AgSbF6
DEC3-87	4.75%	1.49%	45.4%	31.4%	57.6%	PNB latex w/cat and act
DEC3-92	5.01%	1.96%	38.3%	39.2%	63.5%	PNB latex sonicated w/cat and act
DEC3-99	4.85%	2.60%	0.5%	53.6%	53.8%	P(NB-10) latex sonified w/cat and act
DEC3-100	4.71%	0.42%	19.0%	8.8%	10.9%	sonified NB-10 and Styrene
DEC4-01	5.00%	---	---	---	---	PNB latex w/o act or SDS and w/NaCl
DEC4-02	5.00%	---	---	---	---	PNB latex w/o act or SDS
DEC4-03	5.00%	---	---	---	---	PNB latex w/o act or SDS and w/KCl
DEC4-04	5.00%	---	---	---	---	PNB latex w/ Na2SO4 rather than SDS
DEC4-05	5.00%	---	---	---	---	PNB latex w/ nonionic surf and Na2SO4 w/o act
DEC4-06	4.45%	2.22%	0.0%	4.7%	4.7%	P(NB-10) seed PS 2nd stage FRP
DEC4-07 a	4.67%	4.48%	0.0%	95.8%	95.8%	P(NB-10) seed
DEC4-07 b	6.79%	6.02%	0.0%	74.1%	74.1%	P(NB-10) seed PS 2nd stage FRP
DEC4-16	5.02%	2.65%	3.2%	52.8%	54.6%	PNB w/ LiDS w/o act
DEC4-17	5.26%	2.56%	4.0%	48.7%	50.7%	PNB w/ SDS w/o act
DEC4-18	4.69%	2.29%	1.3%	48.9%	49.6%	PNB w/ LiBF4 act
DEC4-20	5.52%	---	---	---	---	PNB w/o act w/ SDecS
DEC4-21	4.86%	2.58%	2.1%	53.0%	54.2%	PNB w/o act w/ SODS
DEC4-22	5.23%	3.32%	3.4%	63.4%	65.7%	PNB w/o act w/STDS
DEC4-24	5.56%	2.20%	2.8%	39.5%	40.7%	PNB w/RDP w/o act
DEC4-25	5.22%	2.87%	2.5%	55.0%	56.4%	PNB w/ Na hexadecane SO3 w/o act

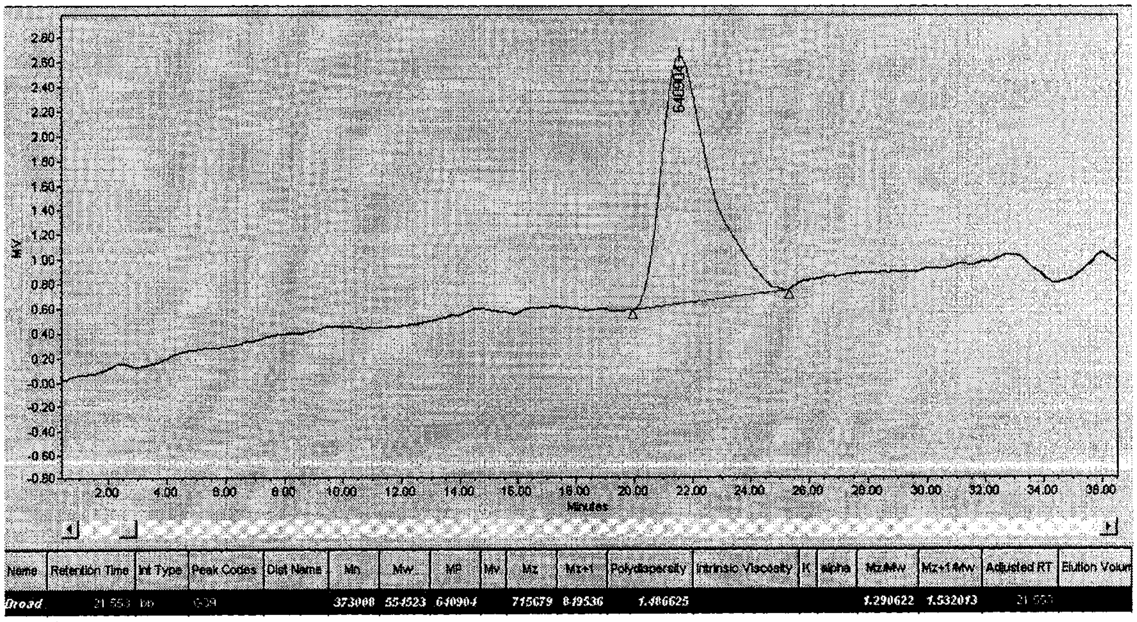
APPENDIX C

Gel Permeation Chromatography



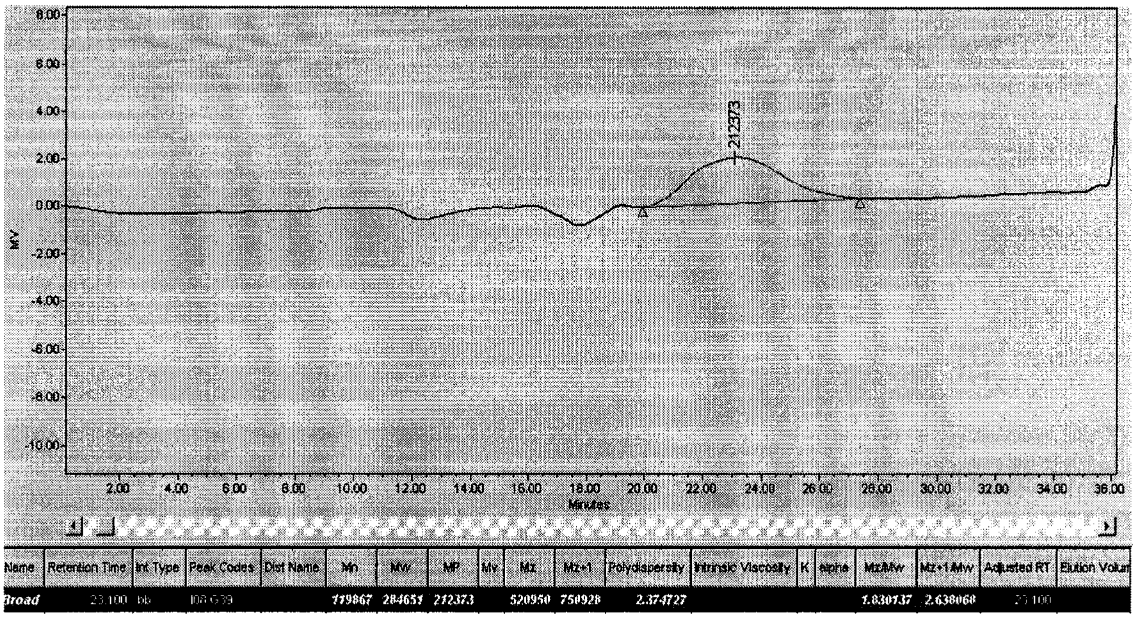
Name	Retention Time	Int Type	Peak Codes	Dist Name	Mn	Mw	MP	Mv	Mz	Mz+1	Polydispersity	Intrinsic Viscosity	K	alpha	Mz/Mw	Mz+1/Mw	Adjusted RT	Elution Volum
Broad	23.163	bb	G37		134223	267393	203065		522979	896799	1.992145				1.955845	3.353865	23.163	

DEC3-23



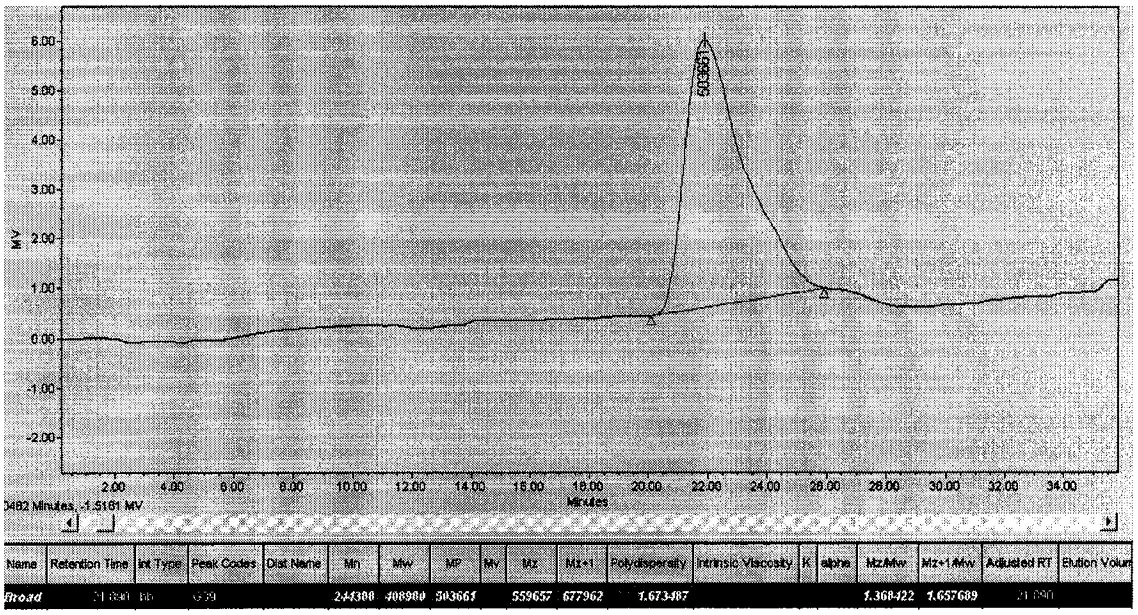
Name	Retention Time	Int Type	Peak Codes	Dist Name	Mn	Mw	MP	Mv	Mz	Mz+1	Polydispersity	Intrinsic Viscosity	K	alpha	Mz/Mw	Mz+1/Mw	Adjusted RT	Elution Volum
Broad	21.553	bb	G39		373008	554523	640904		715679	849536	1.486625				1.290622	1.532013	21.553	

DEC3-26



Name	Retention Time	Int Type	Peak Codes	Dist Name	Mn	Mw	MP	Mv	Mz	Mz+1	Polydispersity	Intrinsic Viscosity	K	alpha	Mz/Mw	Mz+1/Mw	Adjusted RT	Elution Volu
Broad	23.100	bb	I08 G39		119867	284651	212373		520950	750928	2.374727				1.830137	2.638068	23.100	

DEC3-27



Name	Retention Time	Int Type	Peak Codes	Dist Name	Mn	Mw	MP	Mv	Mz	Mz+1	Polydispersity	Intrinsic Viscosity	K	alpha	Mz/Mw	Mz+1/Mw	Adjusted RT	Elution Volu
Broad	21.890	bb	G39		244308	408980	503661		559657	677962	1.673487				1.368422	1.657689	21.890	

DEC3-28