SYNTHESIS, CHARACTERIZATION, AND KINETIC STUDIES OF POLY(DIMETHYLACRYLAMIDE) MACROMONOMER

SYNTHESIS, CHARACTERIZATION, AND KINETIC STUDIES OF POLY(DIMETHYLACRYLAMIDE) MACROMONOMER

By

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ABSTRACT

The work in this thesis focuses on the search for a system that would allow for the controlled anionic polymerization of N,N-dimethylacrylamide. The resulting polymer would serve as a macromonomer equipped with a chain end functional group originated from diallylamine.

Poly(dimethylacrylamide) macromonomers were produced on a laboratory scale by reacting diallylamine with *sec*-butyllithium initiator, followed by the monomer addition. The synthesis was terminated, the polymer product precipitated in hexane, and dried in a vacuum oven at 45°C. The reactions were performed at 0°C
and –77°C in tetrahydrofuran solvent.

The polymerization control was achieved as a means of controlling the molecular weight and stereoregularity of the macromonomer, which in turn dictated solubility of the final product in the reaction solvent. The addition of triethylborane coordinating agent allowed for the polymerization of soluble product. The produced macromonomers characterized with atactic and syndiotactic structure were completely soluble in tetrahydrofuran.

The molecular weights of macromonomers were evaluated by a gel permeation chromatography, GPC. The best results were obtained by using dimethylformamide as a mobile phase and poly(methylmethacrylate) standards.

The macromonomer yield was evaluated by ^{1}H NMR and the stereoregularity by ^{13}C NMR. Although the molecular weight of the macromonomer was under good control, the NMR measurements did not show the best yield control.

The study of the triethylborane coordinating power showed that varying concentration of this ligand affected the solubility of the polymer in the reaction solvent.

The soluble macromonomer was synthesized when triethylborane was in 1.5 molar excess over the initiator concentration. The ^{13}C NMR measurements indicated that 23% of isotactic and atactic structure was required as a borderline for the solubility.

The kinetic measurements performed in a batch reactor proved the livingness of the polymerization system with the propagation rate constant k_{obs} equal to $1.9 \cdot 10^{-3}[\frac{1}{s}]$.

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CHAPTER 1

Introduction

1.1 Properties of *N,N*-dimethylacrylamide monomer and applications of poly(dimethylacrylamide) polymer and its derivatives

Water-soluble polymers are polymers that are soluble in aqueous media by means of ionic or non-ionic polar functional groups. Extensive usage of water-soluble polymers worldwide is estimated at over 5 M t/yr.[1,2]

N,N-dimethylacrylamide monomer is widely used in making block copolymers by free radical polymerization and branch copolymers by grafting techniques. As a colourless viscous liquid with freezing point –40°C, boiling point 171-172°C and relative density 0.965 g/ml, *N,N*-dimethylacrylamide is soluble in water and other polar solvents such as chloroform.[55] It is highly hygroscopic and with LD50 460 mg/kg is considered to be a toxic compound. Polymers made of *N,N*-dimethylacrylamide are inert and have good antibacterial and antiviral properties.[3]

Poly(dimethylacrylamide) and its copolymers prepared by different methods allow applications in many fields. We can identify two general branches of these applications: medical and non-medical. The medical field includes therapeutic, biomedical/prosthetic and pharmaceutical headings.

PDMA has an excellent non-fouling property. The partial rejection of protein adsorption on a grafted surface is achieved by steric hindrance effect due to tethered chains of two methyl groups attached to nitrogen of poly(dimethylacrylamide). A grafted surface has a diffuse structure since body fluids and the polymer are hydrophilic. When proteins are in contact with grafted polymer chains, they are not adsorbed on the surface due to the repulsive force that is generated by the balance of entropic elasticity of the chains and osmotic pressure.[4]

This non-fouling property of PDMA has a wide application potentials since any object exposed to human body, has to be extensively engineered to assure complete compatibility with the human body, one of which is that the implantable device cannot adsorb protein on its surface, otherwise the trombogenesis process can lead to serious clinical problems such as blood cloths leading to death and as a consequence the implant will be finally rejected by the body. This non-fouling property of poly(dimethylacrylamide) can thus be used for engineering surface of catheters, dialysers, vascular grafts, blood containers, and oxygenators.[5]

Another important property of poly(dimethylacrylamide) grafted on the surface of a catheter or a medical diagnostic device such as an endoscope is the reduction of the coefficient of friction. Lubrication of the surface in a hydrated state allows for better flow of the fluids during dialyses or during medical testing. It was found that grafting of poly(dimethylacrylamide) is effective in reducing the friction force.[4]

A number of recent patents refer to applications of grafting *N,N*-dimethylacrylamide as a co-monomer on silicone hydrogel contact lenses.[6,7,8] In order to increase hydrophilicity, a silicone hydrogel contact lens is subjected to plasma treatment with ammonia and butadiene giving a carbon-containing layer and further coating with polymer containing dimethylacrylamide and oxazolin.

Extensive research is being done on the design and synthesis of semipermeable membranes of amphiphilic copolymers including *N,N*-dimethylacrylamide monomer. These highly engineered membranes can be used in manufacturing implantable biological devices. They can encapsulate and immunoisolate biological cells upon introduction into a human body. Hydrophilic segments of the membrane consist of polyacrylates and hydrophobic segments of polyolefins terminated with radicals from acryloyl or methacrylolyl groups.[9]

Kennedy et al.[10,11] invented a small implantable reservoir comprising of a semipermeable membrane that encapsulates pancreatic islets. These devices having a

volume smaller than 1 ml can be injected into a human body and they can be used in the treatment of diabetes. Glucose must permeate through the implant membrane and bind with islet cells. The pancreatic cells can be stimulated to produce insulin upon the reaction with glucose present in the human body. The insulin must diffuse out the device through the semipermeable membrane. The membrane includes an amphiphilic copolymer network with hydrophobic segments synthesised from polyolefins terminated with radicals selected from the acryloyl and methacrylolyl group and hydrophilic segments from polyacrylates. The hydrophobic part is a macromonomer, methacrolyl-capped polyisobutylene and the hydrophilic part is *N,N*-dimethylacrylamide, *N,N*-dimethylaminoethylmethacrylate, and 2-hydroxyethyl methacrylate.

The pharmaceutical application of *N,N*-dimethylacrylamide polymers refers to control drug delivery systems.[1] The ultimate goal of an active reagent drug is to be released in a designated location at a given time. The oral administration of peptide/protein type of drugs is not very efficient using standard drug delivery methods due to enzymatic degradation in the gastrointestinal track. Research on site-specific drug delivery includes studies on biodegradable, pH sensitive hydrogels that are incorporated in the active drug formulation. Yeh and Copeckova synthesized biodegradable and pH-sensitive hydrogels by crosslinking of *N,N*-dimethylacrylamide copolymer precursors.[12]

Hydrogels with the active drug swell gradually passing through the gastrointestinal track, where pH gradually increases from the stomach to the colon. In the colon swelling reaches a point at which crosslinks become accessible to microbial enzymes. The gel is degraded and the drug released. This study is an important step in treating a colon cancer.

In addition to the direct medical applications of poly(dimethylacrylamide), this polymer is used in biodiagnostics. Poly(acrylamide-co-dimethylacrylamide) coatings in capillary electrophoresis allow for high precision DNA sequencing.[13] The dynamic coating ability of polydimethylacrylamide combined with the hydrophilicity of

polyacrylamide gives the copolymer ability to adhere to a glass capillary. Separation ability of such capillaries depends on the molar ratio of the co-monomers.

Non-medical applications of the *N,N*-dimethylacrylamide polymers can be found in adhesives, synthetic fiber industry, paper industry, oil field chemistry,[11] photography and printing. An emulsion of copolymer of *N,N*-dimethylacrylamide and sulphonic acid derivatives is a water-in-oil emulsion where the copolymer is dissolved in the water phase . This hydraulic cement additive is used to control the fluid loss from cement composition that damages structure properties and reduces pumpability of the cement. For off-shore applications the additive is prepared and stored as a suspension of copolymers in oil to prevent settling of solid polymers.[14]

Water-soluble polymers can be used as grafts on other polymer surfaces. The polymer chains get entangled between two substrates and subjected to water and pressure, followed by drying, give excellent adhesive properties of the material. *N,N*-dimethylacrylamide is used in fiber reinforced composites to improve matrix-fiber adhesion.[15] Addition of *N,N*-dimethylacrylamide to epoxy resin compositions gives prepregs (thin sheets of continuous reinforced fibers impregnated with thermoplastic resin used as laminates) an improved cover factor reaching 98.2%.[16]

The paper industry uses *N,N*-dimethylacrylamide as an additive by grafting a cationic starch with (methacryl)amides, anionic vinyl monomers and crosslinkers to improve paper strength.[17] An example of a potential application of *N,N*-dimethylacrylamide in the printing industry is reflected in the recent publication by Santos et al.[18] Poly ethyleneteraphtalate, PET can be modified with dimethylacrylamide to obtain a better incorporation of a blue dye as shown by stretching of the carbonyl and vinyl bond of the monomer (IR spectroscopy).

1.2 Potential applications of poly(*N,N*-dimethylacrylamide) macromonomer

The purpose of this research is to synthesize a macromonomer of poly(dimethylacrylamide). All the details regarding the objectives of this study will be detailed in section 1.3. This section outlines potential applications of the studied macromonomer with reference to the fields in which poly(dimethylacrylamide) and its random copolymers are currently used. A number of these applications are presented in section 1.1.

The applications of the macromonomer are determined by the structure of poly(dimethylacrylamide), its end-functional group, the methods of synthesis, the mechanisms of processing the polymer, and the physical and chemical properties of this macromonomer. Purity of the final macromonomer as well as costs of production will also influence the applicability of the macromonomer in various fields. The biomedical field will require the highest purity polymer with a well determined structure with no monomer residue and other reagents used in the polymerization process. The oil field industry would probably accept lower purity materials but at significantly reduced costs.

First of all, poly(dimethylacrylamide) synthesized by anionic polymerization can give a polymer with a very narrow molecular weight distribution. The presence of a double bond as chain end functional group allows for further polymerization by a free radical mechanism to prepare a block/comb copolymer. This fact gives flexibility in the design of macromolecules with amphiphilic properties tailored to a particular usage.

Previously described polymer grafts applied as coatings or adhesives are prepared by coupling reactions or graft polymerization. Grafting *N,N*-dimethylacrylamide on a substrate is often done by a graft polymerization method using γ-rays, ozone, glow discharge, or UV radiation. Poly(dimethylacrylamide) as a macromonomer could be used as a surface modifier by a readily conducted chemical coupling reaction instead of grafting by γ-rays or UV radiation by means of a double bond present on terminus. Surface modification done by this method would be more uniform since the

macromonomer has a very low polydispersity. This would be desired in the case of medical implants such as catheters, artificial veins. This uniformity in coating would probably improve antitrombogenetic properties of the implants or instruments used in dialyses. They could last longer due to rejection of proteins that have a tendency to coagulate around a foreign body.

Another aspect of the macromonomer application is related to the increased flexibility in the design of block/comb copolymers. In an amphiphilic network, the hydrophilicity can be controlled by regulating the molecular weight of the macromonomer. Instead of a random incorporation of a hydrophilic monomer into the structure of a block copolymer, the uniform macromonomer could give a better engineered amphiphilic structure.[19] Swellability of hydrogels whether in contact lenses or in site-specific drug delivery systems can be controlled by varying molecular weight of the macromonomer.

Looking at the synthesis and processing of polymers and also at the economics, batch polymerization is more desirable than semi-batch and continuous processes. Additional costs in semi-batch and continuous processes are associated with the equipment and process control instrumentation. A semi batch process is implemented when reactivity ratios for particular monomers are significantly different. This difference in reactivity ratios causes copolymer composition drifting and gives a non-uniform copolymer product when synthesized in a batch process. Graft copolymers for biomedical applications often consist of different molecular weight monomers.[20] When polymerized by a free radical mechanism in a batch process, the final product is non-uniform due to different reactivity ratios. By adjusting the macromonomer molecular weight to decrease the difference in co-monomer sizes, the reactivity ratios could be regulated. The replacement of N,N-dimethylacrylamide with the macromonomer of poly(dimethylacrylamide), reactivity ratios could potentially be closer and batch processing would give an uniform copolymer.

1.3 Research objectives

The overall objective of this study is to synthesize poly(dimethylacrylamide) macromonomer by "living" anionic mechanism. Such a macromonomer can be used to make block/comb copolymers. The anionic polymerization is selected in this research since this type of synthesis gives well defined low polydispersity polymer product. Low polydispersity gives high probability that the polymer is more uniform in terms of its properties and behaviour in different media.

Preliminary experiments carried out under the standard conditions at which most anionic polymerizations are performed, i.e. low temperature, clean system, pure reagents, sufficient mixing, solvent, initiator, and monomer, did not produce polymers with projected properties. The synthesized polymers were not soluble in the reaction solvent THF and when characterized, did not give predefined chain properties such as molecular weight or polydispersity.

This step led to defining a detailed set of objectives for further study. The plan of the research was based on an extensive literature search and the critical analysis of the system to understand the chemistry and mechanisms of the polymerization. Once the reaction system and purification methods for solvent and monomer were developed, a number of potential chemical compounds were selected and tested to give solubility of the polymer in THF during the process.

The next objective was to find at least one coordinating agent that when added to the process, would give soluble in the reaction medium polymer. It was also planned to study any influence of this compound on the macromonomer structure. A set of experiments was defined to study the influence of this coordinating agent on the final macromonomer properties.

The final two goals of this research were to characterize the macromonomer by various analytical methods and to perform kinetic measurements of the macromonomer

polymerization. The objective of the kinetic investigation was to find a range of temperatures at which reasonable time interval samples could be taken and to determine the reaction rates.

1.4 Thesis outline

Chapter 1 has been a review of properties of *N,N*-dimethylacrylamide monomer and applications of poly(dimethylacrylamide) polymer with emphasis given to biomedicine. It is structured such that the first part deals with fields of applications and the second part is an attempt to suggest potential applications of the newly synthesized macromonomer of poly(dimethylacrylamide). The structure of the second part is based on properties and mechanisms of the reactions.

Chapter 2 gives some background on anionic polymerization with emphasis on acrylates and methacrylates polymerization. Since solubility of the polymer in the reaction solvent is related to tacticity of the polymer, some introductory information is given to polymer stereoregularity. Following introductory statements, a detailed description of the reaction chemistry and mechanisms of the polymerization pertaining to the studied system is included in this chapter.

The experimental part of the thesis is included in Chapter 3 and Chapter 4. Upon introduction, which defines system requirements, reagent preparation, and experimental conditions, screening of the coordinating agents and selection of the functional agent is described. This chapter also describes the investigation of the influence of coordinating agent on tacticity of the macromonomer. All the analyses are done based on characterization results of the macromonomer using various analytical and instrumental methods, which are described in Chapter 3 together with the discussion pertaining to all experimental results.

In Chapter 4 the kinetic investigation of the reactions is performed and reaction rates determined.

The thesis is summarized in Chapter 5. Some recommendations are made for further work in the area.

CHAPTER 2

Chemistry and Mechanisms of the Polymerization

2.1 Introduction

Polymerization reactions can be classified into two groups: condensation polymerization and addition polymerization, as proposed by Carothers. This classification is based on the comparison of the molecular formulae of a polymer with that of the monomer from which the polymer is synthesized. Addition polymerization produces polymers with the repeat unit having the same molecular formulae to the monomers from which they are formed.[21] This relation does not hold in the case of polycondensation in which an elimination of a small molecule occurs during the process.

A different approach allows for identifying step growth and chain growth polymerizations. Chain growth polymerization requires initiation, a reaction between the monomer and an initiator to start the chain growth. Depending on the mechanism of the reaction, addition polymerization can be subdivided into radical, ionic (cationic, anionic) and catalytic (Ziggler-Natta) polymerization.

Anionic polymerization was utilized in this research study. Selection of this polymerization type was dictated by the final properties of the designed macromonomer. Polymers produced by the anionic mechanism are characterized by predictable molecular weight, narrow molecular distribution, controlled stereochemistry, functional termination capability, and block copolymer synthesis. Monomers that undergo anionic polymerization have electron withdrawing constituents. This electron withdrawing group stabilizes the propagating anionic centre. Many anionic polymerizations do not undergo termination reactions. This is a major difference from free radical polymerization. In many instances, a reaction is called "living polymerization".[22] This is defined as a polymerization without permanent chain transfer. An active center will not terminate during the polymerization. The reaction stops when monomer molecules are exhausted,

and the polymer has polydispersity close to unity. This almost monodisperse polymer is produced due to a rapid generation of active centers. All the chains grow essentially for the same period of time. The following equation represents the relationship between polydispersity and degree of polymerization for a living system.[23]

Equation 2.1 Polydispersity in living anionic polymerization

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + \frac{Dp}{(Dp+1)^2}$$

$\frac{\overline{M}_w}{\overline{M}_n}$ is the polydispersity, and Dp the degree of polymerization

This equation shows that as the molecular weight of a polymer increases, the polymer polydispersity approaches unity. Polymers with low molecular weight and narrow molecular weight distribution require a special care to experimental details.

Living polymerization can be achieved in solvents such as tetrahydrofuran or dioxane which do not terminate propagating species by chain transfer. Usually a relationship between the molecular weight and conversion will indicate the character of polymerization. A straight line with a given slope reflects a living polymerization.

A variety of initiators are available in anionic polymerization. Some of these initiators are metal amides, alkoxides, cyanides, phosphines, amines, or organometallic compounds such as butyllithium.[22] Lithium based initiators are extensively used in initiations due to their solubility in hydrocarbon solvents.

The first step in an anionic polymerization is initiation followed by propagation. Once the monomer is added to growing chains, the reaction can be deliberately terminated by deactivating the active center. Figure 2.1 shows the steps involved in an anionic polymerization.

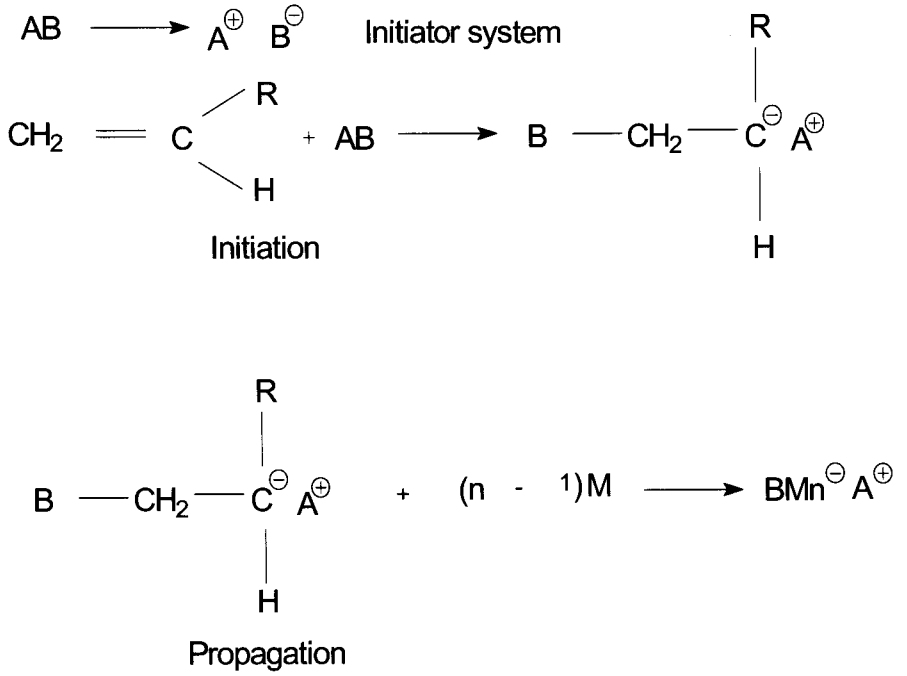


Figure 2.1 Mechanism of an anionic polymerization

An additional requirement imposed upon a macromonomer is the presence of a terminal group that is capable of further polymerization. Therefore, there must be a double bond(s) present at one end of individual polymer chains. An incorporation of a functional group into the initiator system can provide this requirement. The synthesis of macromonomers with terminal vinyl group by living anionic polymerization can be divided into two groups:[24]

a) initiation with a vinyl containing initiator system
b) end capping with a vinyl containing capping agent

This research project reports work done on the synthesis of macromonomers by the first route, initiation with a vinyl containing initiator system. Examples of compounds that contain vinyl group(s) available for incorporation into the initiator system are shown in Figure 2.2.

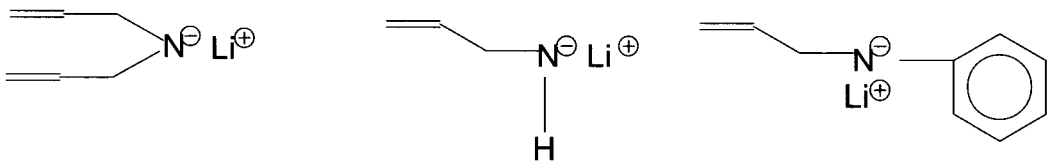


Figure 2.2 N substituted allylaminolithium

A number of conditions must be met for a successful living anionic polymerization. The reaction system must be free of any impurities including glassware, reaction solvent, initiator, monomer(s), and any other reagents used in the process. Once these conditions are met, the polymerization of vinyl monomers such as styrene in THF can give a low polydispersity polymer product with a predicable molecular weight, assuming that reaction takes place at a sufficiently low temperature. The low temperature prevents side reactions that would terminate propagating chains. The situation is more complicated when alkyl acrylates, acrylamides or alkyl methacrylates are used as monomers. The presence of a carbonyl group in the monomer structure makes the system more vulnerable to termination.

For methyl methacrylate and related polar monomers, termination reactions can take place during the initiation step.[25] The initiator can react with the monomer at the carbonyl group of the ester. As a result, a ketone and an alkoxide will be formed.

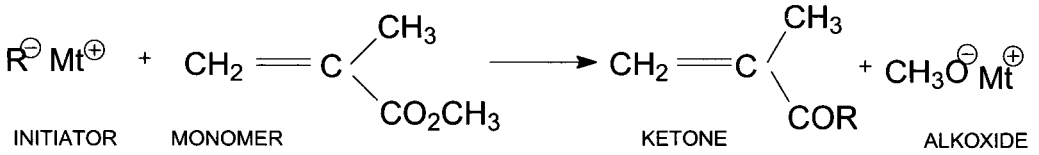


Figure 2.3 Termination by the initiator attack on the carbonyl moiety of the monomer

This termination will reduce the concentration of the active initiator and result in a higher-than-calculated molecular weight. If we consider *N,N*-dimethylacrylamide , the potential deactivation reactions can occur by:[26]

a) intra- or inter-molecular attack of the propagating anionic center on the amide carbonyl group as in the case of alkyl methacrylate (Figure2.3)

b) deprotonation of the methine proton in the polymer forming a stabilized carbanion

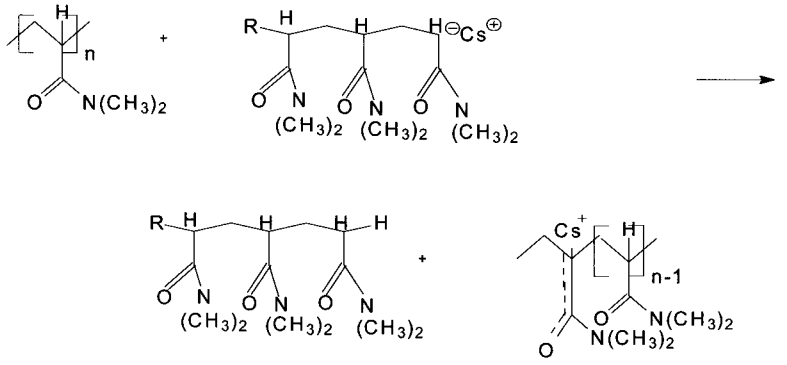


Figure 2.4 Termination by the deprotonation of the methine proton

c) deprotonation of the methyl or methylene groups α to the amide nitrogen forming a dipole stabilized anion

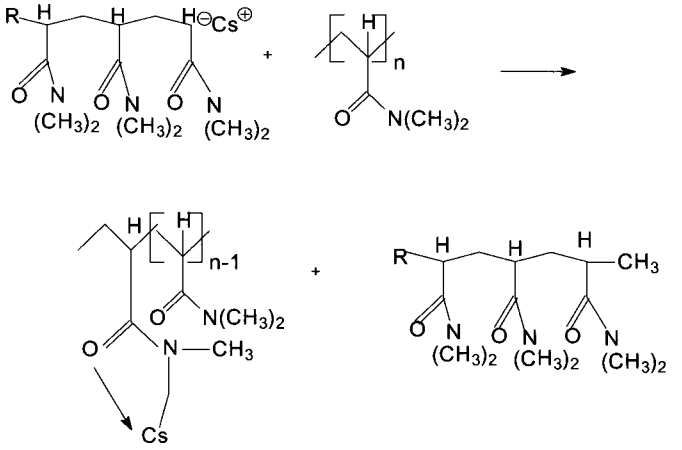
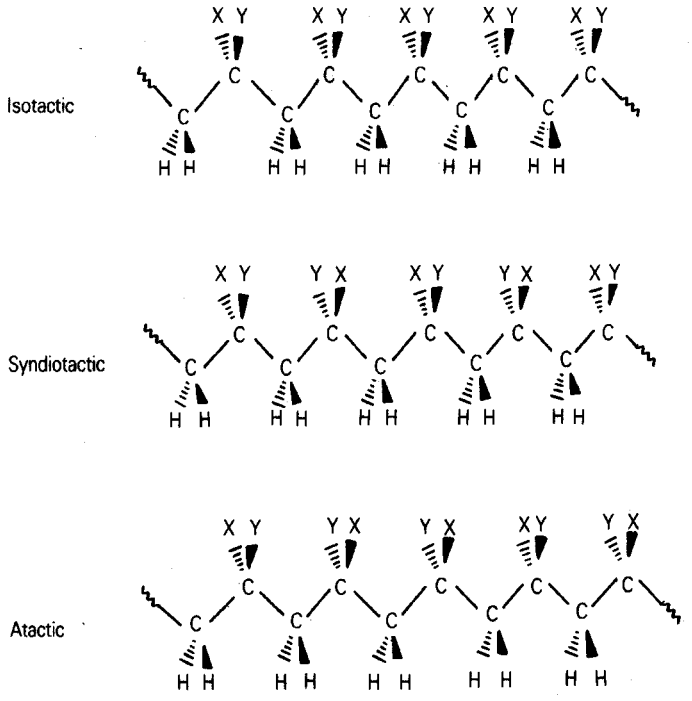


Figure2.5 Termination by the deprotonation of methylene group

Stereoregularity of the polymerization plays an important role in the solubility of polymers in reaction solvents. It also determines final properties of the synthesized material.

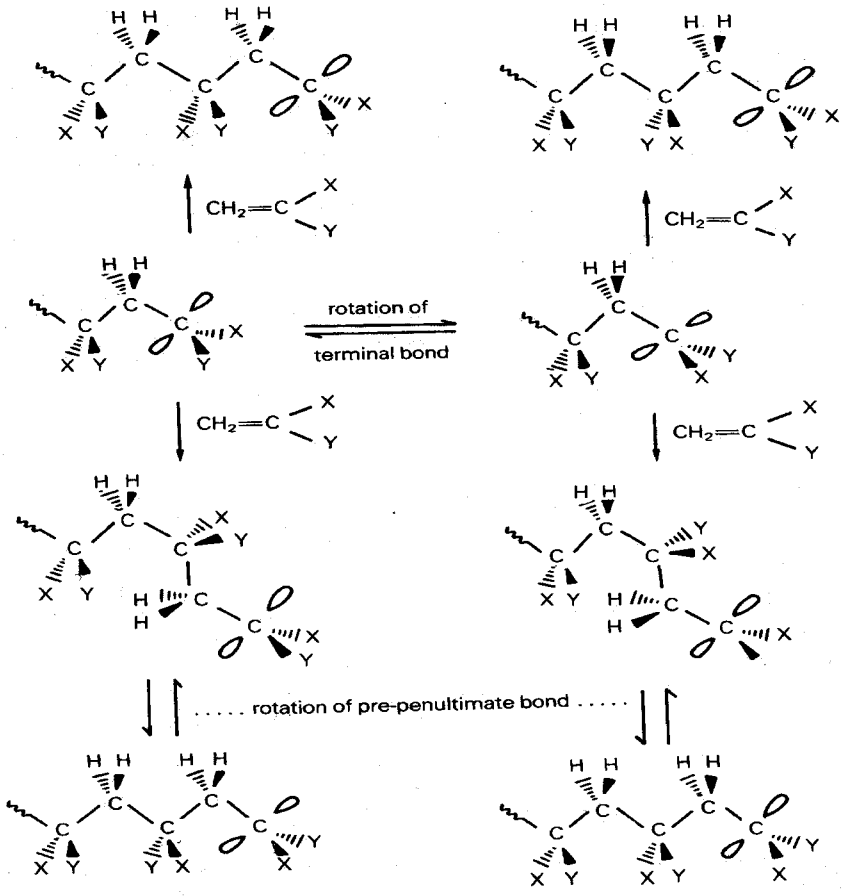
Poly(dimethylacrylamide) can have isotactic, syndiotactic or atactic microstructures that determine the physical properties of the polymer. Figure 2.6 shows three types of stereochemical forms of vinyl polymers.[28]



For Poly(dimethylacrylamide) $X = H$ *and* $Y = CON(CH_3)_2$

Figure 2.6 Stereoregular forms of vinyl polymers[28]

The tacticity of a polymer is controlled by the stereochemistry of propagating center. In the carbanionic polymerization electron withdrawing substituents cause a resonance of anions. There is a planar arrangement of the groups about the terminal active carbon atom (sp^2 hybridization – coplanarity).[47] The constituent configuration in the polymer molecule is determined by the way in which the monomer is added to the growing active chain in the propagation step. The orientation of the substituent groups on the terminal active carbon atom of the penultimate repeat unit and the face of the planar active center are critical in determining the mode of addition. Usually electronic repulsion between similar substituent groups gives preference to a syndiotactic mode. Lowering reaction temperature can increase syndiotacticity in the anionic polymerization, whereas high temperatures give atactic polymers.[28] Figure 2.7 shows the stereochemistry of propagation.[28]



For Poly(dimethylacrylamide) *X = H and Y = CON(CH$_3$)$_2$*

Figure 2.7 Stereochemistry of propagation[28]

Anionic polymerization of alkyl methacrylates is dependant on the counterion, solvent, and temperature.[29] Syndiotacticity is thermodynamically favoured over isotacticity in the anionic polymerization of methyl methacrylate. The free energy differences are so small that the formation of stereoregular chains must be kinetically controlled.[30] The kinetic control arises from the differences in free energies of activation during the addition of monomer unit to form an isotactic or syndiotactic dyad. The rate constant ratio (k_{iso}/k_{syndio}) and the free energy of activation show that small differences in activation energy can lead to large differences in stereochemistry of the propagation. Isotacticity increases with the increase of k_{iso}/k_{syndio} and with the increase of free energy of activation.[29]

2.2 Reaction chemistry

The research study was conducted on *N,N*-dimethylacrylamide that was polymerized into poly(dimethylacrylamide) macromonomer with the end functional group consisting of two double bonds generated from diallylamine. The polymerization was accomplished by anionic mechanism. The reaction steps are shown in Figure 2.8

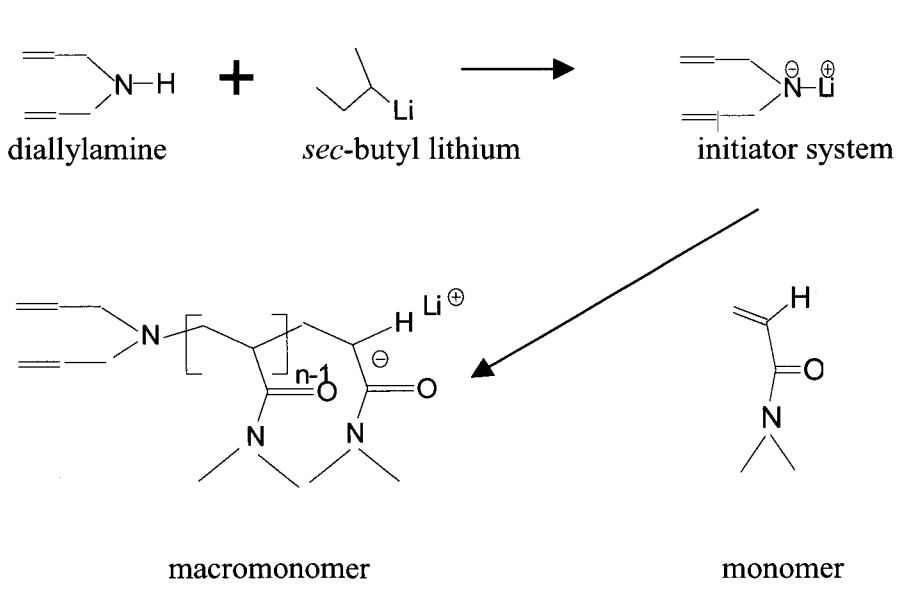


Figure 2.8 PDMA macromonomer synthesis- reaction chemistry

In the first step, the initiator system containing two allyl groups was synthesized. The *sec*-butyllithium initiator was reacted with diallylamine in tetrahydrofuran THF solvent. Various temperatures were used in the experiments ranging from –76°C to 0°C. *N,N*-dimethylacrylamide was added into the initiator system to start polymerization. The polymer was terminated with methanol that was injected into the system at the end of the process. Depending on the purpose of the experiment, temperature, time intervals for addition of the reagents, and termination times were varied. The details regarding experiment conditions will be outlined in chapter 3, section 3.2.

Poly(dimethylacrylamide) can be used as a macromonomer in a free radical polymerization to form well-defined block/comb copolymers. In order to incorporate

poly(dimethylacrylamide) into the comb structure with another polymer such as polyacrylamide, double bonds as the chain end functional group have to be activated by quaternization in this case.

2.3 Mechanisms of the polymerization of N,N-dimethylacrylamide by lithium diallylamine

The preliminary synthesis of poly(dimethylacrylamide) macromonomer in which the initiator system with chain end double bond was reacted with the monomer at 0°C in THF gave an insoluble polymer in the reaction solvent. The reaction was instantaneous and the product was a form of solid blocks. An extensive literature search in respect the polymerization of alkyl acrylates and alkyl methacrylates provided insight into the details of reaction mechanisms of the studied system.

The lack of polymer solubility in THF at experiment conditions can be attributed to tacticity. Poly(dimethylacrylamide) can have a tactic or atactic structure. The tactic structure can be isotactic or syndiotactic. Lithium-initiated polymerization of *N,N*-dimethylacrylamide leads to a highly isotactic crystalline polymer which is only partially soluble in water, in contrast to the amorphous water-soluble syndiotactic polymer made by free radical polymerization.[31]

The polymerization mechanism can be analyzed by looking into the initiation and propagation. These two steps determine the polymer structure. Fast initiation and slow propagation are desired in the polymerization of *N,N*-dimethylacrylamide. If the initiation is fast, all active anion chains have the same time frame for propagation. This can give low polydispersity of the final polymer. Slow propagation is preferred and it leads to a polymer that is soluble in THF. As described in chapter 3, sections 3.3 and 3.4, the preliminary experiment without coordinating agent gave insoluble in THF product. The reaction was completed within few seconds. The product precipitated shortly after

monomer injection. The kinetic investigations described in chapter 4, section 4.2 revealed that slow propagation can give soluble in THF polymer.

The anionic polymerization of alkyl methacrylates or alkyl acrylates is governed by complicated kinetics due to the presence of different types of active species. Each species propagates with a different rate giving multimodal distributed polymer. Active species tend to aggregate into dimers or tetramers, which in turn slows down the rate of addition of monomer units to the growing chain. Besides aggregates, there can be contact ion pairs, solvent separated ion pairs and free ions.[29] Each of these types contributes to the propagation with different rates. Therefore, the goal of the study is to suppress this variability to one type of species at the initiation stage so that the polymer can grow uniformly.

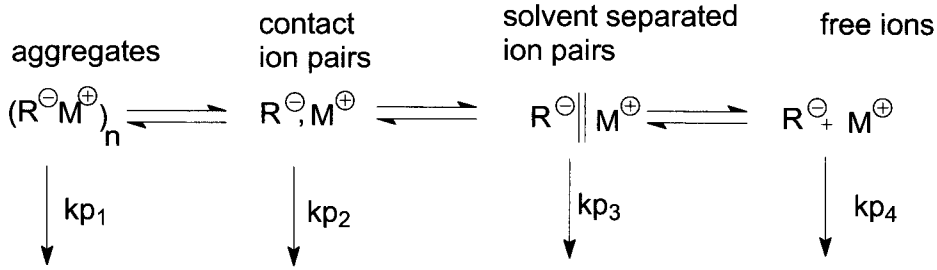


Figure 2.9 Winstein spectrum of active species [48]

The aggregation of active species is a limiting factor in the availability of initiator molecules for propagation. If the equilibrium between aggregates and free ion pairs is more toward to the aggregates, the polymer molecular weight can be significantly increased. A part of the initiator molecules are "dormant" and do not participate in the polymerization. The monomer is added to the reduced concentration of active initiator species resulting in a higher-than-calculated number-average molecular weight, Mn.

The initiator aggregation needs to be inhibited. One possible approach is to use a coordinating agent or to increase solvation of the active species. The type of reaction solvent will have an influence on the aggregation of active species. Higher polarity of the

solvent gives a lower degree of aggregation. The degree of aggregation of lithium ester enolate and related compounds is shown in Table 2.1.[48]

Table 2.1 Aggregation of initiator species in solvents of different polarity

Compound	Degree of aggregation Benzene	Degree of aggregation THF
$(CH_3)CLiCO_2C_2H_5$	6.6	3.5
$(CH_3)_2CLiCO_2C(CH_3)_3.(CH_3)_3COLi$	2.8	1.8
$C_4H_9Li.(CH_3)_3COLi$	3.7	1.8

THF as a polar solvent gives lower degree of aggregation of active species than apolar benzene.

Solvation of active species can also be controlled by the size of the cation used in the active species. If the size of the cation increases, the interaction between the cation and anion decreases. If the size of the cation decreases, the solvation power in a polar solvent increases. Hogen-Esch et al.[26] studied the influence of cation size on the structure of poly(dimethylacrylamide) and poly(acryloylmethylpiperazine) in anionic synthesis of polymer samples having narrow molecular weight distribution. They discovered that polymerization in the presence of Cs^+ as counterion has homogenous character and yields polymers with controlled molecular weights and narrow molecular weight distribution when compared to lithium based initiators.

The use of coordinating species opens a new route for polymerization called "ligated anionic polymerization (LAP)". Coordinating agents play an important role in the initiation and propagation. These agents can be classified into three groups:[32]

- μ-type ligands form polycentric bonding with the metal ester enolate: metal alkoxides, aluminum alkyls, inorganic salts such as LiCl
- δ-type ligands form coordinative complexes with the metal counterion of the active species: crown ethers, kryptands
- μ/δ-type ligands form μ- type and δ-type interactions with the active species, polyether metal alkoxides such as lithium 2-(2-methoxyethoxy) ethoxide

The role of coordinating species in the initiation step can be understood as reducing the interactions between the counterions. Separating the anion from cation by the incorporation of ligand weakens the bonding, thus decreasing the aggregation.

In order to control the molecular weight of the polymer the propagation rate during the polymerization should be slow. If the propagation is fast, the molecular weight distribution cannot be controlled properly. Insufficient mixing in relation to the fast propagation in the reaction flask produces polymer with high polydispersity. Another factor indicating the need for slow propagation is the high termination probability of the alkyl acrylates or alkyl methacrylates by undesired reactions of the growing chain with the carbonyl group of the monomer when fast propagation occurs (Figure 2.3). The possible solution for this problem is to use coordinating agent or capping agent.

Capping agents are incorporated into the initiator. They increase the bulkiness of the initiator, hindering the propagation step. A capping agent will protect the initiator from reacting with the carbonyl group that would terminate the growing chain otherwise.

Shen et al.[24] were able to control the polymerization of *N,N*-dimethylaminoethyl methacrylate (DMAEMA) and synthesized macromonomer with predictable molecular weight and narrow molecular weight distribution by incorporating *N,N*-dimethylacrylamide and *tert*-butyl methacrylate as capping agents into the initiator system.

Ballard et al.[34] were successful in controlling the polymerization of methyl methacrylate using lithium aluminum alkyls. The combinations of organolithium and tetraorganoaluminates can form a group of initiator complexes in toluene that when anionically polymerized can give controlled poly(methyl methacrylate) at temperatures 0-40°C. The lithium and aluminum components must have alkyl groups which have cross sectional areas as large as possible. This bulkiness of the initiator system will selectively give a reaction of growing chain with the carbon-carbon double bond of the monomer.

The coordinating power of μ-type, δ-type, or μ/δ-type ligands can be used to stabilize growing carbanions. Lithium halides such as lithium chloride (LiCl), lithium alkoxides, diethylzinc (Et_2Zn), triethylborane (Et_3B), and crown ethers have been successfully used as coordinating agents in anionic polymerizations of alkyl methacrylates and alkyl acrylates in polar and apolar solvents.[35-44]

The addition of a Lewis acid such as diethylzinc or triethylborane to the anionic polymerization of *N,N*-dimethylacrylamide in THF leads to polymers with the narrow molecular weight distribution and predictable molecular weight in quantitive yields.[40,42] The experiments showed that the Lewis acid coordinated with the enolate anion to produce a stable propagating species resulting in polymer having predetermined structure.

The coordinating agents not only slow down the propagation rate, but also dictate stereoregularity of the synthesized polymers. The polymer solubility of the polymer in various solvents is governed by the polymer structure. In contrast to isotactic poly(dimethylacrylamide), atactic and syndiotactic polymers are soluble in tetrahydrofuran. Atacticity can be related to fast propagation in which monomer units are added randomly to the growing chain. To prevent stereoregularity at slow propagation rates, the carbanion has to be sufficiently separated from the metal cation, since the mode of monomer addition depends on the distance between opposite charges.[45]

The solubility of polymer in reaction solvent allows for controlling the polymerization process. Therefore the aim of this thesis is directed to find an appropriate system that would yield atactic or syndiotactic polymer which would guarantee the polymer solubility in THF. Table 2.2 summarizes published experiments that have produced the polymers soluble in reaction solvents. Different initiator systems, monomers, coordinating agents and their ratios to the initiator, and solvents were used.

Table 2.2 Summary of the referenced solubility experiments

MONOMER	INITIATOR	T(°C)/time(min)/ X(%)	LIGAND	LIGAND/IN ITIATOR	TACTIVCITY	PD	SOLVENT	REFFERE NCE
DMA	DPPLi/Na	+30/90/95	Et3B	2.3:1	S,A	1.05	THF	40
DMA	DPPLi/Na	-78/60/96	Et2Zn	12:1	S.A	1.14	THF	40
MMA	Ph2CHNa	-20/5/97	DB-18-crown-6	1:1	S,A 9.8%isotactic	1.05	Toluene	44
MMA	Ph2CHNa	-20/5/97	DB-18-crown-6	2:1	S,A 7.5%isotactic	1.04	THF	44
DMAEMA	SBuLi+DAA	-78/120/98	Capping DMA,t-BuMA	2:1	Soluble in THF	1.07	THF	24
DEA	Ph2CHK	+30/60/97	Et3B	2.3	S.A	1.07	THF	40
DMA	Bu2Mg	-50/15/--	----------		S,A	3.2	Toluene	41
DMA	Bu2Mg	----------	----------		S,A	----	THF	41

Et3B triethylborane

Et2Zn diethylzinc

DPPLi 1,1-diphenyl-3-methylpentyllithium

Ph2CHNa(K) diphenylmethylsodium(potassium)

DAA Diallylamine

s-BuLi sec-Butyllithium

Bu2Mg dibutylmagnesium

DB-18-crown-6 dibenzo-18 crown ether-6

X – conversion

S- syndiotactic

A- atactic

The first two positions in this table show that *N,N*-dimethylacrylamide can be polymerized into an atactic and syndiotactic polymer product that is soluble in THF.

1,1-Diphenyl-3-methylpentyllithium initiator used in the experiments carries a higher mass when compared to sec-butyllithium used in this research study. Triethylborane and diethylzinc used as coordinating agents allow for the successful synthesis of soluble polymers in THF. The molar ratios of these ligands to the initiator are different, 2.3:1 for triethylborane and 12:1 for diethhylzinc, indicating that triethylborane has a stronger coordinating power than diethylzinc.

The polymerization of methylmethacrylate (MMA) as shown in Table 2.2, position three and four, was accomplished with diphenylmethylsodium with the presence of crown ether (dibenzo-18 crown ether-6). A number of smaller crown ethers were also used in the experiments,[44] but did not allow control of the process as good as in dibenzo-18 crown ether-6 case. Matching the size of crown ether diameter to that of metal cation as well as its phenyl substituents is critical in the successful control of this polymerization process.

The result of dimethylaminoethylmethacrylate polymerization into a macromonomer with diallylamine and *sec*-butyllithium is shown in the fifth line in the Table 2.2. Dimethylacrylamide in one set of experiments and *tert*-butylmethacrylate in the second set were incorporated into the reactions as capping agents. These agents increased the bulkiness of the initiator and prevented undesired reactions of the initiator with the carbonyl group of monomer. Eliminating any of these capping agents did not allow for the controlled polymerization of the macromonomer.

Dibutylmagnesium was used in another set of experiments as an initiator. The magnesium cation in the initiator system as a larger counterion than lithium allowed for the polymerization of an atactic and syndiotactic soluble macromolecule.

2.4 Summary of literature overview.

A number of acrylic, methacrylic, and acrylamide monomers used to synthesize low polydispersity polymers were investigated in many scientific journals. Methyl methacrylate, dimethylacrylamide, dimethylaminoethylmethacrylate, and diethylacrylate monomers with lithium, sodium, and caesium based initiators are the most frequently studied systems. The reaction mechanisms derived from the extensive experimentation allow for considering following aspects of polymerization in this research study:

- initiation and propagation mechanisms

- coordinating agent influence on polymer solubility
- polymer stereoregularity
- a cation versus anion interaction
- a multitude of propagating species
- active species aggregation
- growing chain termination

In order to have a low polydisperity polymer, the initiation should be fast. The fast initiation is possible if initiator molecules are deaggregated. The presence of coordinating agent and the solvent type can help to separate these molecules.

The propagation should be slow. The slow propagation can be achieved by incorporating a coordinating agent into the process that will not only shield the carbonyl group of the monomer from the initiator attack, preventing termination, but also will separate counterions sufficiently to control stereoregulraity of the product.

The monomer addition mode will determine the polymer solubility in THF. Isotactic polymer will not dissolve in THF, whereas atactic and syndiotactic polymer will be soluble in THF. This mode of addition can be controlled by establishing the distance between counterions. This distance will change, depending on the type and concentration of the coordinating agent used. Although fast propagation would favour atactic polymer structure, the short distance between counterions would dictate an isotactic addition.

The multitude of active species present in a reaction vessel leads to the multimodally distributed polymer due to different propagation rates for each active species. Coordinating power of ligands can depress this active species variability and establish a single type of an active species.

In each published case in regards to dimethylacrylamide monomer, polymerization led to the product that was not capable of further polymerization. The novelty of this study is the synthesis of the macromonomer, a product that can be further

polymerized to make copolymers. The preservation of the chain end functional group is a critical step in this process. The advantages of having a controllable polymerization process for poly(dimethylacrylamide) macromonomer can be found in the flexibility of regulating the amphiphillic properties of copolymers or in improving coating abilities.

The literature overview provides the useful information that allow for defining the polymerization system. Evaluation of this system can give answers to, how well poly(dimethylacrylamide) macromonomer synthesis can be controlled.

CHAPTER 3

Synthesis and Characterization of Macromonomers

3.1 System requirements and reagent preparation

Anionic polymerization gives polymers with the narrow molecular weight distribution and controlled molecular weight. The major disadvantage of this polymerization type is a strict requirement for the purity of the system and reactants. The reaction has to be free of any active hydrogen containing impurities that can originate from reactor surface walls to the monomer composition. Water and inhibitors in monomer solutions are the major contributors to chain termination. Some polymerizations involving 1,1-diphenylethylene added to the initiator in THF can be useful not only as a capping agent in block copolymerizations but also serve as impurity indicators. When the system is free of impurities, a red color indicates the presence of the living anions. This is not the case in an anionic polymerization of *N,N*-dimethylacrylamide with *sec*-butyllithium and diallylamine. There is no such color indication. Therefore special attention must be given to the preparation of the reactants in order to control the polymerization of this macromonomer.

Tetrahydrofuran THF (Aldrich, reagent grade) was purified prior to the experiments. The solvent was transferred to a 1000 ml 3-neck, round bottom glass flask equipped with a Teflon coated stirring bar. The headspace of the flask was purged with argon for 30 minutes in order to remove oxygen. Several grams of sodium metal in kerosene were precut into small chunks and added to the flask. Approximately 0.5 g of benzophenone (Aldrich) was added to the mixture of THF and sodium and allowed to stir under argon. It is important to use an excess of sodium to prevent the distillation of benzophenone. The benzophenone served as an indicator of purity of THF. The mixture was allowed to reflux for several hours under constant purge of argon. A dark purple color indicated that the solvent was free of any impurities. It was collected in the receiving flask as shown in Figure 3.1.

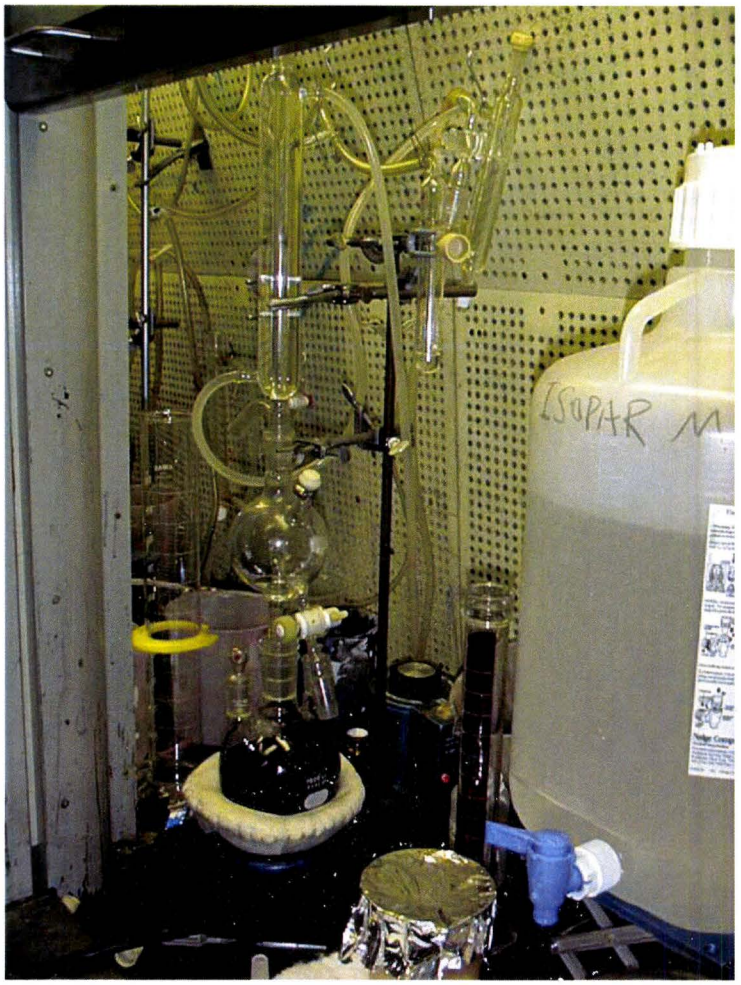


Figure 3.1 THF distillation apparatus

The dark purple color visible in the flask was associated with the formation of sodium/benzophenone ketyl as indicated in Figure 3.1.[33]

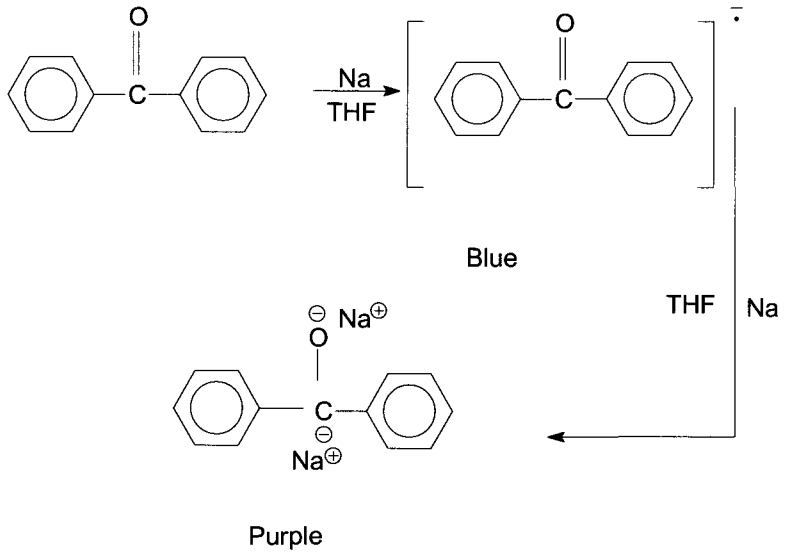


Figure 3.2 Chemistry of THF purification

Initially a radical anion is formed giving a blue color. The complete conversion to the dianion indicates THF purity by dark purple color. If the dry THF was exposed to air, it would turn green and then yellow. To bring the system back to dryness, additional small quantities of sodium and benzophenone were added and THF refluxed under the argon purge.

Sec-butyllithium (Aldrich) was purchased as a 1.3 molar solution in hexane. It was used as received without further purification. Due to the temperature sensitivity, the initiator was stored in a refrigerator. Its concentration was determined prior to experiments and the quantity added for initiation was adjusted depending on the molecular weight requirement and current molarity. The determination of initiator concentration was done by a backtitration method in hexane. An erlenmayer flask was cleaned, oven baked and cooled down to room temperature under nitrogen purge. It was rinsed with hexane. After transferring 75 ml of hexanes (Aldrich), adding a magnetic Teflon coated stirring bar, and 1~2 mg of the indicator 2,2-biquinoline (Aldrich), the glass flask was capped with a rubber septum and purged with dry nitrogen for five minutes. Prepurified nitrogen was obtained by passing the gas through two Dryrite columns. One drop of *sec*-butyllithium being assayed was added to the flask to obtain a yellow color indicating the purity of the system. 0.3~1.5 mL of the initiator was

transferred to the flask by a syringe giving a dark yellow color of the solution. It was followed by a titration with 1 molar 2-butanol. 2-butanol solution was prepared prior to the titration by adding anhydrous 2-butanol (Aldrich) to hexane in the volumetric flask that was cleaned and oven baked. The end point of titration was reached when the solution's yellow color disappeared. The sample calculation is shown in Table 3.1.

Table 3.1 Assay of *sec*-butyllithium

Assay of *sec*-butyllithium 3-18-02

Initiator	**sec-butyllithium**
lot #	AO11127JI
Density [g/ml]	0.769
	2-butanol
Density [g/ml]	0.669
Conc. [mol/l]	0.89

Titration:	Weight [g]	Volume [ml]	concentration [mol/l]
sec-butyllithium	0.30	0.39	**0.887**
	0.22	0.29	**0.884**
	0.42	0.55	**0.974**
2-butanol	0.26	0.39	
	0.19	0.28	
	0.40	0.60	

c1*v1=c2*v2 c1=(c2*v2)/v1
c1-concentration of sBuLi
c2-concentration of 2-BuOH
v1- volume of s-BuLi Average conc.= 0.915
[mol/l]

Based on three titrations, the average initiator concentration in hexane was 0.915 mol/l. This value is different from the 1.3 molar solution that was shipped. Extended storage of butyllithium initiator causes gradual decomposition of active species and therefore it must be analyzed prior to experiments. This particular batch of the initiator was stored in a refrigerator for more than six months and it had been frequently used.

Sec-butyllithium is a pyrophoric material and requires special handling precautions. When exposed to air or moisture it spontaneously ignites. All the equipment used in handling of the initiator was clean and dried in an oven. It was purged with prepurified

nitrogen prior to use. The container with *sec*-butyl lithium and triethylborane was pressurized to 10 kPa to facilitate transfer to the syringe. To prevent material exposure to air and moisture, all operations were performed with sealed containers and new polypropylene or glass syringes.

N,N-dimethylacrylamide (Aldrich) was purified by the vacuum distillation over calcium hydride. It was stored in a freezer. The monomer purification apparatus is shown in Figure 3.3

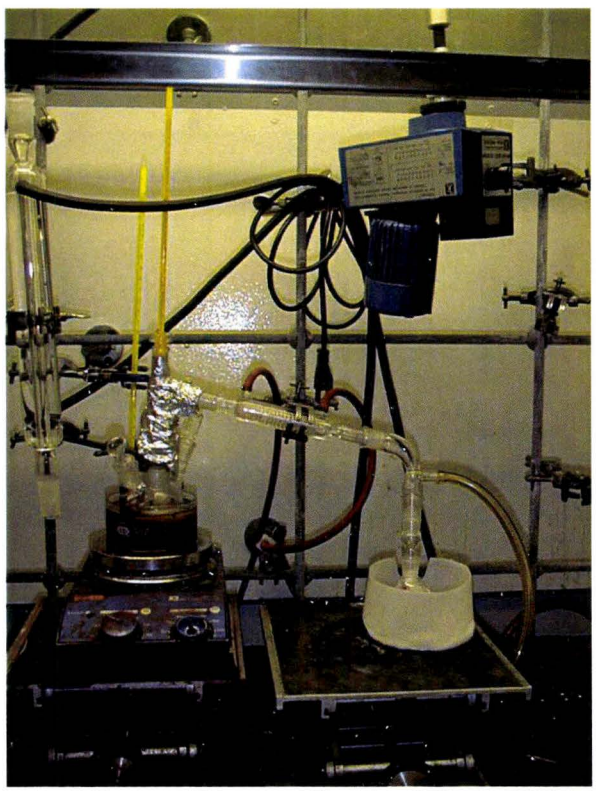


Figure 3.3 Monomer purification apparatus

A 70-100 ml of *N,N*-dimethylacrylamide was transferred to a clean, oven-baked glass round-bottom flask equipped with a magnetic stir bar. This was followed by an addition of 0.7-1.0 g of calcium hydride powder (Aldrich). Hydrogen gas evolution was visible in the flask after the addition of calcium hydride. The monomer was stirred for 24 hours under dry nitrogen purge. The flask was connected to the vacuum distillation apparatus as shown in Figure 3.3. The monomer was distilled at an oil bath temperature of 65°C and vapour temperature of 40~45°C at an estimated 5 mmHg vacuum. The first

distillate cut was discarded and the main fraction was collected in a small glass round bottom flask. Approximately 1 g calcium hydride chunks were placed in a receiving flask to assure complete dryness of the monomer during storage. The flask containing an uninhibited and dried monomer was capped with a rubber septum, pressurized to 10 kPa and wrapped with Parafilm. It was stored in the freezer for further use. The monomer was analyzed for water content prior to use by the Karl Fisher titration.

Preparation of *N,N*-diallylamine reagent (Aldrich) required removal of inhibitors and water from freshly supplied material. It was treated similarly to the monomer by adding 0.5~1.0 g of calcium hydride to 50-100 ml of diallylamine transferred to a glass round bottom flask equipped with a stirring bar. Similar to the monomer treatment, a vigorous hydrogen evolution was visible in the flask after the addition of drying reagent. The flask contents were mixed for 10-15 hours under a limiting prepurified nitrogen purge. Due to the high volatility of this reactant, the nitrogen was turned off over night and resumed 2-3 hours prior to the distillation. The flask was connected to the vacuum distillation apparatus as shown in Figure 3.4.

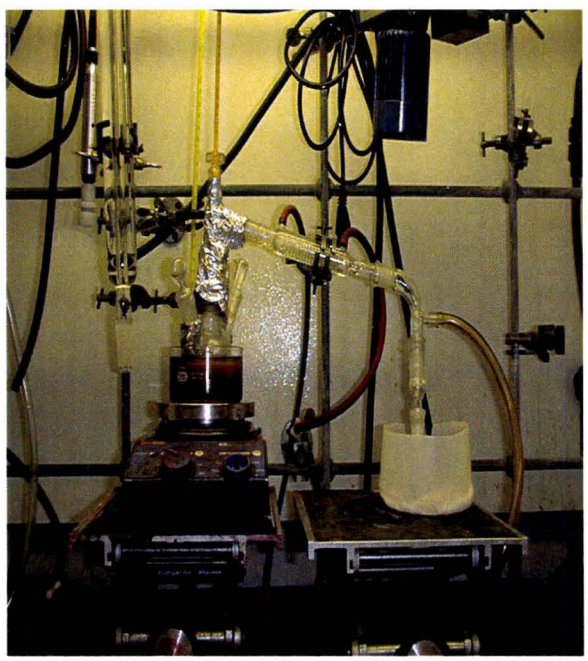


Figure 3.4 Vacuum distillation apparatus for diallylamine

Diallylamine was distilled at an oil bath temperature of 45-70°C and vapour temperature of 30-40°C at the variable vacuum adjusted by a tri-way valve. The vacuum reduction was necessary to prevent contamination of the distillation apparatus with calcium hydride transferred by the excessive boiling ("burping") of diallylamine. The first distillate cut was discarded and the main fraction was collected in a small glass round bottom flask. Approximately 1 g of calcium hydride chunks were placed in the receiving flask to assure complete dryness of the diallylamine during the storage. The flask containing uninhibited and dried monomer was capped with a rubber septum, pressurized to 10 kPa and wrapped with Parafilm. It was stored in the freezer. Diallylamine boils at 82°C at atmospheric pressure, but to prevent the possibility of damaging the reactant structure, the vacuum distillation method of purification was undertaken.

Triethylborane (Aldrich) was supplied as a 1 molar solution in THF and it was used as received without additional purification. A tight sure-seal cup (Aldrich) assured the absence of oxygen in the headspace of the container. After each use, the oxygen present in the bottle was displaced by dry nitrogen. The reactive nature of triethylborane did not allow for the application of additional purification methods.

There were a number of experiments in which crown ether 15-crown-5 (Aldrich) and hexamethyltriethylenetetraamine HMTETA (Aldrich) were used as coordinating agents. They were prepared as 0.3~0.5 molar solutions in THF. Their purification was completed by adding 1 % wt calcium hydride into a small glass flask and stirred with a small bar under pre-purified nitrogen purge for 12~15 hours. The flask contents were allowed to settle for 2~3 hours. Required quantities of the reagents were filtered prior to experiments. A 0.2 um Teflon syringe filters served as filter medium.

Methanol (Aldrich) was used to terminate anionic polymerization experiments. It was used as received.

3.2 Experimental conditions.

All experiments were performed in glass round bottom flasks. The scale of the experiments was reduced to 50 ml in order to reduce the potential monomer and initiator exposure to impurities especially to moisture. If one mol of the polymer having number-average molecular weight Mn of 6000 g/mol was subjected to one mole of water (18 g/mol), this one mole of polymer would be totally terminated. If the initiator molecule has a molecular weight 140 g/mol and is exposed to one mol of water causing the termination, the ratio 18/(140+18)=0.11 shows, how critical the purity of the system is in any anionic polymerization.

One-neck, 50 ml, round bottom glass flasks were cleaned prior to the polymerization and placed in an oven at 110°C. Teflon coated stirring bars were also solvent cleaned and oven baked together with the flasks. The flasks were removed from the oven on the day of the experiment and capped with rubber septa. The glass surface was subjected to reaction with trichloromethylsilane TCMS to remove any hydroxy groups residing inside the flasks. The flasks were rinsed with TCMS and drained after 5 minutes of agitation. A complete removal of trichloromethylsilane was assured by acetone rinse. The glassware was heated to 130°C by partial immersion in an oil bath. After removal from the oil bath, it was evacuated and pressurized with vacuum and dry nitrogen four times. This treatment assured a complete dryness of the system.

The cooled and pure THF solvent collected in the receiving flask of the distillation apparatus was transferred to reaction flask fitted with rubber septum by argon pressure using a cannula. The amount of THF in the flask was determined gravimetrically. The concentration of the monomer was in a range of 10~15 %wt. Following the solvent transfer, a predetermined quantity of diallylamine was injected to the flask by a glass microsyringe. The quantity of this reagent was very critical in the polymerization. It determined the quantity of any other reactants in the experiment. Therefore the transfer

of diallylamine had to be done by weight with the usage of an analytical balance with accuracy to four decimal places.

The transfer of diallylamine was followed by the cooling of the reaction flask under continuous stirring. Depending on the temperature requirement for a particular process, various solvent combinations were used as cooling baths. A detailed list of these combinations is shown in Table 3.2.[46]

Table 3.2 Solvent baths for heating and cooling

System	°C	System	°C
p-Xylene/N_2	13	Carbitol acetate/CO_2	-67
p-Dioxane/N_2	12	t-Butyl amine/N_2	-68
Cyclohexane/N_2	6	Ethanol/CO_2	-72
Benzene/N_2	5	Trichloroethylene/N_2	-73
Formamide/N_2	2	Butyl acetate/N_2	-77
Aniline/N_2	-6	Acetone/CO_2	-77
Cycloheptane/N_2	-12	Isoamyl acetate/N_2	-79
Benzonitrile/N_2	-13	Acrylonitrile/N_2	-82
Ethylene glycol/CO_2	-15	Sulfur dioxide/CO_2	-82
o-Dichlorobenzene/N_2	-18	Ethyl acetate/N_2	-84
Tetrachloroethane/N_2	-22	Ethyl methyl ketone/N_2	-86
Carbon tetrachloride/N_2	-23	Acrolein/N_2	-88
Carbon tetrachloride/CO_2	-23	Nitroethane/N_2	-90
m-Dichlorobenzene/N_2	-25	Heptane/N_2	-91
Nitromethane/N_2	-29	Cyclopentane/N_2	-93
o-Xylene/N_2	-29	Hexane/N_2	-94
Bromobenzene/N_2	-30	Toluene/N_2	-95
Iodobenzene/N_2	-31	Methanol/N_2	-98
Thiophene/N_2	-38	Diethyl ether/CO_2	-100
3-Heptanone/CO_2	-38	n-Propyl iodide/N_2	-101
Acetonitrile/N_2	-41	n-Butyl iodide/N_2	-103
Pyridine/N_2	-42	Cyclohexene/N_2	-104
Acetonitrile/CO_2	-42	Isooctane/N_2	-107
Chlorobenzene/N_2	-45	Ethyl iodide/N_2	-109
Cyclohexanone/CO_2	-46	Carbon disulfide/N_2	-110
m-Xylene/N_2	-47	Butyl bromide/N_2	-112
n-Butyl amine/N_2	-50	Ethyl bromide/N_2	-119
Diethyl carbitol/CO_2	-52	Acetaldehyde/N_2	-124
n-Octane/N_2	-56	Methyl cyclohexane/N_2	-126
Chloroform/CO_2	-61(-77)	n-Pentane/N_2	-131
Chloroform/N_2	-63	1,5-Hexadiene/N_2	-141
Methyl iodide/N_2	-66	i-Pentane/N_2	-160

Reactions at –77°C were conducted in a dry ice/acetone bath. It was prepared by adding small lumps of dry ice to acetone with small excess of dry ice. A temperature of 0°C was achieved by crushing lumps of ice formed from deionized water. The temperature of the bath was monitored by a thermometer that was immersed in the bath. Any temperature changes were adjusted by adding small fractions of ice or dry ice, depending on the bath type.

Acetonitrile/dry ice and acetone/deionized water baths gave –42°C and –10°C respectively.

The initiator system consisting of *sec*-butyllithium and diallylamine was synthesized by injecting a defined volume of initiator to reaction flask with THF under continuous agitation. The amount of the initiator added depended on the projected number-average molecular weight of polymer and the initiator concentration. The initiator concentration was determined by titration prior to experiment as described in Table 3.1. A sample calculation of the initiator used is shown in Table 3.3.

Table 3.3 Stoichiometry of the initiator

Polymerization of N,N-dimethylacrylamide
Initiator charge calculation

M1	moles of DAA	0.0003	C2 x V=M2
M2	moles of s-BuLi	0.0003	1.3xV=0.0003
C2	molarity of s-BuLi	1.3	V=0.0003/1.3= 0.000231[L]
			= 0.231 [ml]

V volume of s-BuLi

The table shows that 0.231 ml of 1.3 molar *sec*-butyllithium needed to be added to have 0.0003 mol initiator charge.

After initiator addition, a predetermined quantity of the coordinating agent was added to the flask by a clean and dry syringe. The amount of this reagent varied based on the goal of each experiment. A sample calculation of the quantity of triethylborane

ligand used is presented in Table 3.4. In this example the ratio of triethylborane to *sec*-butyllithium was assumed to be two to one.

Table 3.4 Stoichiometry of the coordinating agent

M1	Moles of DAA	0.0003
M2	Moles of s-BuLi	0.0003
M3	Moles of Et3B	0.0006
C3	Concentration Et3B	1.00

C3 x V3 = M3

1.00 x V3 = 0.0006

V3 = 0.0006[L]

V3 volume of Et3B = **0.6 [ml]**

For a 0.0003 mol initiator loading, 0.6 ml of 1.0 molar triethylborane coordinating agent needed to be injected to the system to have a 1:2 ratio of initiator to ligand.

Time intervals between additions of diallylamine, coordinating agent, initiator and monomer were varied and were dependent on the goal of each experiment. These details will be revealed in section 3.5.

The monomer was added after the initiator system was established. A clean and dry polypropylene syringe was purged with dry nitrogen and a predetermined mass of monomer was transferred to the syringe. The monomer was injected to the reaction flask and the polymerization was started.

The amount of *N,N*-dimethylacrylamide added in each polymerization was based on the required number average molecular weight of the macromonomer and the amount of the initiator injected to the reactor. A sample calculation of the monomer quantity added is shown in Table 3.5.

Table 3.5 Stoichiometry of the monomer

Polymerization of N,N-dimethylacrylamide
Monomer charge calculation

Macromonomer with Mn = 6000[g/mol]

Mn = g monomer / moles of initiator

Moles of diallylamine DAA =	0.0003
Moles of initiator s-BuLi =	0.0003
Moles of coordinating agent Et3B =	0.0006

g monomer = Mn x moles of initiator = **1.8**[g]

The projected macromonomer of poly(dimethylacrylamine) with the number-average molecular weight of 6000 g/mol and the charge of 0.0003 mol of the initiator, 0.0003 mol of diallylamine, and 0.0006 mol of triethylborane coordinating agent, required 1.8 g of the monomer to be injected to the system.

Propagation proceeded within a predetermined time frame ranging from two to four hours, depending on the experiment objectives. The polymer was terminated by injecting 0.5 ml of methanol and precipitated in hexanes. The non solvent was decanted after 30 minutes and the polymer dried in the fume hood for 10 hours. The drying was continued for 24 hours in the vacuum tray oven at 45°C. The dry polymer was transferred to a glass bottle.

3.3 Methodology of the experimentation.

The preliminary synthesis of poly(dimethylacrylamide) macromonomer at –77°C gave an isotactic product insoluble in THF. The failure to make the predefined macromonomer supported by the extensive literature research led to a defined set of objectives and methodology of the experimentation. Understanding mechanisms of the reaction allowed for:

- selecting reagents to be used as coordinating agents in a search for the control of stereoregularity
- testing experiment reproducibility
- analysing the influence of the selected coordinating agent on the stereoregular structure of the polymer
- selecting methods for polymer analysis
- analysing the kinetics of the polymerization

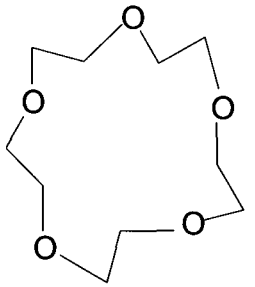
3.4 Experimental work - screening coordinating agents

The coordinating agents classified in Section 2.3 influence the mechanisms of polymerization in different ways. Depending on the type of chemical compound, they can coordinate with cations or enolate propagating anions. The strength of the interaction depends on the type and concentration of such an agent. Their role is to disassociate the initiator molecules, accelerating initiation and slowing the propagation. The dual functions of the coordination in the propagation prevents undesired propagating chain termination and insures sufficient separation of counterions in the initiator system. This separation is critical in controlling the stereoregularity of polymer. The counterions are separated from each other by a distance that does not implicate the monomer addition mode to propagating chain. It results in an atactic product.

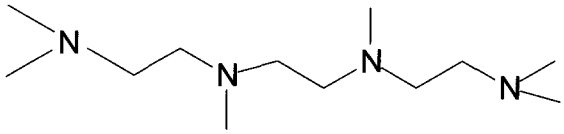
The first part of experimental work was related to the screening of a number of coordinating agents to produce a polymer soluble in THF. The extent of this part was influenced by the compound availability and the time frame assigned to these experiments. Once a particular coordinating agent passed the screening process, it was used in the entire study. The following agents were used in the screening:

- crown ether 15-crown-5 (15-c-5)
- hexamethyltriethylenetetraamine (HMTETA)
- hexamethylenetetraamine (HMTA)
- triethylborane (Et3B)

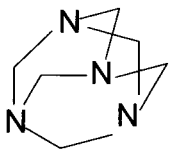
Figure 3.5 shows coordinating agents used in screening experiments.



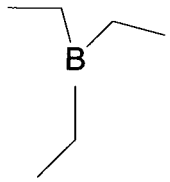
15-c-5



HMTETA



HMTA



Et3B

Figure 3.5 Coordinating agents

In addition to the coordinating agents tested, the initiator system was changed from *sec*-butyllithium (s-BuLi) to dibutylmagnesium (Bu_2Mg) to investigate the effect of cation size in the initiator system on the stereoregularity of polymer. The summary of screening experiments is shown in Table 3.6.

Table 3.6 Screening coordinating agents

Experiment number	Temperature [°C]	Initiator	Coordinating agent	Ratio coord. agent:initiator	Solubility in THF
PDMA-1	-77	s-BuLi	5-c-15	1:1	insoluble
PDMA-2	-77	s-BuLi	-	1:1	insoluble
PDMA-3	-77	s-BuLi	HMTETA	1:1	insoluble
PDMA-4	-77	s-BuLi	HMTETA	5:1	insoluble
PDMA-5	-77	s-BuLi	HMTETA	5:1	insoluble
PDMA-6	-77	Bu2Mg	-	-	insoluble

PDMA-7	0	Bu2Mg	Et3B	2:1	insoluble
PDMA-8	0	s-BuLi	Et3B	2:1	soluble

s-BuLi	*sec*-butyllithium initiator
Bu2Mg	dibutylmagnesium initiator
5-c-15	crown ether
HMTETA	hexamethyltriethylenetetraamine
Et3B	triethylborane

The polymer molecular weight was determined by GPC measurements in THF in this part of the research study. This will be discussed in section 3.6. The projected number-average molecular weight was equal to 5000 to 7000 g/mol.

Out of eight experiments only one produced polymer product that was soluble in THF. The remaining systems gave isotactic, insoluble products in the form of physical gels. It is important to notice that although the polymers were not soluble in THF, a small fraction of the product, not visually detectable after precipitation in hexane was formed. This fact was concluded based on GPC in THF analyses of the polymer. A part of polymer sample must be dissolved in THF to be able to measure Mn by GPC in THF.

Crown ether 5-crown-15 used as the coordinating agent for lithium cation did not shield the cation sufficiently and the experiment produced an insoluble polymer. The choice of this reagent was determined based on the information quoted by Sunil Varshney and Robert Jerome.[44] They were able to control the anionic polymerization of methyl methacrylate MMA in THF by incorporating crown ethers into the systems. They studied different crown ethers and their ability to create a steric barrier blocking the space area around the metal cation. They concluded that by matching the size of the crown ether with metal cation, they could synthesize an atactic and syndiotactic polymer. A one-to-one initiator to crown ether ratio is sufficient to control polymer solubility in some cases. If crown ether is smaller than metal cation and the cation can not fit into the crown ether opening, then a higher crown ether to initiator ratio is required. A "sandwich"

structure between ions in the initiator system must be formed to separate cation from anion sufficiently to bring solubility of the product in THF.

The crown ether 5-c-15 used as a coordinating agent in the poly(dimethylacrylamide) macromonomer synthesis did not produce an expected result. The insolubility of the macromonomer in THF can be attributed to the incompatibility of crown ether with Lithium cation. There was no sufficient cation shielding by the coordinating agent. The one-to-one coordinating agent to initiator ratio did not allow for a good ion separation to improve polymer solubility in THF (syndiotactic and atactic structure).

The second experiment, PDMA-2 shows that without any coordinating agent the interaction between anion and cation in the initiator system is significant and dictates the mode of the monomer addition to growing chain. The polymer is not soluble in THF and has an isotactic structure.

The selection of multidentate amines as coordinating agent in controlling anionic polymerization of acryl amides was an alternative to crown ethers. According to Xie and Hogen-Esch[33], addition of complexing agent *N,N,N',N'*-tetramethylethylenediamine for lithium counterion improves the solubility of the polymer in THF, as a result of formation of metal complexes which decrease the polymer chains stereoregularity.

Hexamethyltriethylenetetraamine HMTETA used to achieve the solubility of poly(dimethylacrylamide) macromonomer did not produce a soluble in THF polymer product. The polymer precipitated within a few seconds after the monomer was added to the reaction vessel. Shortly after monomer addition with coordinated lithium based initiator system, the precipitated product was synthesized indicating isotacticity of the polymer. As indicated in Table 3.6, changing ratio of HMTETA to initiator from one-to-one, to five-to-one still produced an isotactic polymer. The coordinating power of HMTETA was not sufficient to produce a soluble-in-THF material.

Experiments PDMA-6 and PDMA-7 were conducted with dibutylmagnesium, Bu_2Mg, as an initiator and triethylborane, Et_3B, as the coordinating agent respectively. Bu_2Mg was reacted with diallylamine, DAA to form chain end functional group capable of further polymerization. The change of the initiator system which replaced lithium with magnesium was a new alternative to investigate. Yakubovich [41] and Hogen-Esch [33] anionically polymerized *N,N*-dimethylacrylamide with calcium and magnesium containing initiators. NMR spectra obtained by Yakubovich, where Bu2Mg was used as initiator, contained signals corresponding to hetero- and syndiotactic triads. In both experimental cases, PDMA-6 and PDMA-7, the synthesized polymer products were insoluble in THF, indicating the ineffectiveness of magnesium as counterion to sufficiently separate the propagating anion from cation, so that the cation does not control stereoregularity of the growing polymer chains.

A soluble polymer was achieved in PDMA-8 experiment in which *sec*-butyllithium was reacted with diallylamine with the presence of triethylborane at 0°C. The monomer coordinated with triethylborane and yielded an atactic and syndiotactic polymer. This was the starting point to further investigate the system in terms of the concentration of the coordinating agent on the polymer tacticity and reaction kinetics.

3.5 Experimental work - testing reproducibility and changing process variables

The purity of the system and reactants required for anionic polymerization indicate the necessity for testing reproducibility of the experiments. Table 3.7 shows the number-average molecular weight and yield of polymer in three consecutive and fourth runs performed in a one month interval, when the experiments were performed.

Table 3.7 Reproducibility testing

Experiment number	Mn by GPC in THF [g/mol]	Yield [%]	Date of exp.
PDMA-9	4430	100	12. 13. 01
PDMA-10	4490	100	12. 14. 01
PDMA-11	4730	99	12. 15. 01
PDMA-20	4480	100	1. 09. 02

The experiments were conducted at 0°C with initiator *sec*-butyllithium coordinated with triethylborane with one-to-two the initiator to coordinating agent ratio.
The results show that the batch reactor is a reliable means for studying the mechanisms and kinetics of PDMA polymerization. The results show good reproducibility. The theoretical number average molecular weight of the macromonomer was equal to 6100 to 6200 [g/mol]. Although the theoretical value of Mn was different from the measured ones, the results were consistent. The Mn measured in THF for each of these polymer samples is lower than a theoretical value by 25-30%. The discussion regarded this reduction will be included in the GPC measurement section of this thesis (3.6).

In order to have good control over the polymerization process a number of experiments were conducted to investigate the influence of various variables that might influence the macromonomer structure. In the experiments PDMA-12 to PDMA-17 and PDMA-21 to PDMA-24, the concentration of Et_3B coordinating agent was varied to see if there was any influence of the ligand concentration on the macromonomer tacticity. The reactor loading was increased in PDMA-18, PDMA-19, and PDMA-20 experiments. The polymer concentration in THF was increased from 13% to 23%. Also in these three experiments the monomer addition rate as well as time intervals between initiator, coordinating agent, and monomer additions were varied.

Since the macromonomer was characterized by GPC and NMR, a detailed discussion of the influence of these variables on polymer properties will be included in the next section of this chapter. The kinetic measurements done in PDMA-24 to PDMA-29 will be discussed in Chapter 4.

3.6 Polymer characterization by GPC measurements

3.6.1 Experimental work - GPC measurements

A number of GPC analyses were carried out in this research study with two types of GPC columns. The GPC in THF solvent was done using STYRAGEL columns in series.[52] GPC in DMF with lithiumbromide was done in ULTRASTYRAGEL columns.[52] The column descriptions are shown in Table 3.8 and 3.9.

Table 3.8

GPC-THF columns

	STYRAGEL
Pore size	Effective Molecular Weight Range
100 A	50-1500
10^3 A	200-30000
Linear	2000-10 million

Table 3.9

GPC-DMF columns

	UltraSTYRAGEL
Pore size	Effective Molecular Weight Range
100 A	50-1500
10^3 A	200-30000
10^4 A	5000 - 500000 million

This section deals with GPC data in relation to the search for the best measurement system and will show an influence of process variables on the molecular weight of the macromonomer. To demonstrate that the polymerization is a controlable process, an accurate determination of the polymer molecular weight is critical. The number average molecular weight, weight average molecular weight, and molecular weight distribution were determined by Waters 2000, the GPC instrument equipped with RI detector, at 30°C, with 1.0 ml/minute elute flow rate. Narrow polystyrene (Polysciences) and narrow polymethylmethacrylate PMMA standards (American Polymer Standard Association) were used to generate calibration curves.

Two instruments were used to measure the polymer molecular weight, one located at McMaster University in Hamilton and the second one at XRCC. A series of analyses were done using both facilities at different conditions in order to find the best measurement parameters. The polymer samples were prepared as 0.3 wt% and 4.0 wt% solutions in THF and in DMF with the addition of 0.01 molar lithium bromide, LiBr solution to eliminate any interaction of the polymer with column packing. Data were recorded and processed using the Windows based Millenium 2.0 software package.

The number average molecular weight, weight average molecular weight, and polydispersity of macromonomers were originally measured in THF. Table 3.10 shows the results of GPC measurements with theoretical Mn presented in the second column, measured Mn in the third, polymer polydispersity in the fourth, and purpose of the experiment in the fifth column.

Table3.10 GPC analyses in THF with polystyrene standards

Experiment number	Theoretical Mn	Mn (THF)	Polydispersity PD	Purpose
PDMA-1	6170	4110	1.13	Screening
PDMA-2	6160	4220	1.20	Screening
PDMA-3	6170	4190	1.22	Screening
PDMA-4	5100	4210	1.12	Screening
PDMA-5	4760	4260	1.12	Screening
PDMA-8	6000	4930	1.20	Screening
PDMA-9	6200	4430	1.20	Reproducibility
PDMA-10	6130	4490	1.20	Reproducibility
PDMA-11	6190	4730	1.19	Reproducibility
PDMA-12	6470	5030	1.29	Et3B ratio 1.5:1
PDMA-14	5870	6040	3.25	Et3B ratio 1:1
PDMA-15	6000	8210	2.2	Et3B ratio 1:1
PDMA-17	6000	15600	8.87	Et3B ratio 0.5:1
PDMA-18	5980	4760	4.08	High reactor loading/fast addition of monomer
PDMA-19	6330	4730	1.15	High reactor loading/Process conditions
PDMA-20	5900	4480	1.13	High reactor loading/Process conditions

Screening - search for coordinating agent and initiator to obtain polymer soluble in THF

Reproducibility - repeated experiments at identical conditions

Et3B ratio #:# - triethylborane to initiator ratio

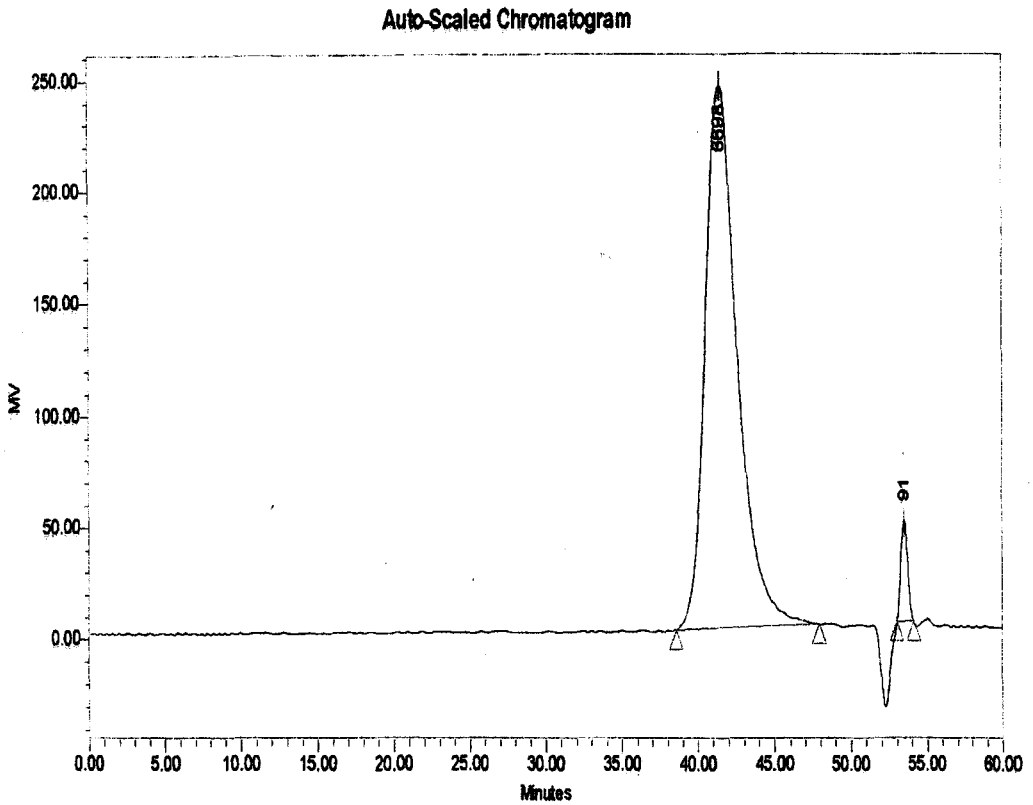
High reactor loading - increased monomer concentration from 15 % to 25 %

Fast addition of monomer - fast monomer addition rate ~1g/second (~0.3 g/second standard rate)

Process conditions - monomer addition 15 minutes after Et3B injection (60 minutes standard procedure)

There is a significant difference between the theoretical and measured Mn. The measured values are smaller than the calculated ones. The relative difference oscillates in a range of 70-75%. This difference is consistent in the screening and reproducibility experiments (PDMA-1 to PDMA-11). The polydispersity is in a range of 1.12 to 1.20. A sample GPC chromatogram is shown in Figure 3.6.

SampleName	PDMA-12	Sample Type	Broad Unknown
Vial	13	Date Acquired	1/10/2002 12:35:53 AM
Injection	1	Acq Method Set	GPC
Injection Volume	150.00 ul	Processing Method	5351
Channel	410	Date Processed	1/11/2002 11:47:27 AM
Run Time	60.0 Minutes		



GPC Results

	Retention Time	Mw	Mn	Polydispersity	MP	Mz
1	41.477	6504	5026	1.294103	6698	7835
2	53.480				91	

Figure 3.6 Sample GPC in THF chromatogram (PDMA-12)

The experiments PDMA-12 to PDMA-17 show the significant difference in theoretical and measured values of Mn. The purpose of these experiments was to investigate the influence of coordinating agent on tacticity of the macromonomer by varying the ratio of coordinating agent (triethylborane) to the initiator. The polydispersity of the polymer increased with the decrease of coordinating agent concentration. The number-average molecular weight could not be controlled without the coordinating agent. The polymer precipitated shortly after the monomer addition, inhibiting mixing. The lack of appropriate mixing did not allow for the system homogeneity, resulting in zones of different monomer concentrations in the reactor.

In experiment PDMA-17, where the ratio of coordinating agent to initiator was 0.5 to 1. The polydispersity reached 8.87 with the Mn equal to 15600 g/mol in this experiment. The propagation was suppressed by inadequate mixing, giving rise to such a high polydispersity. The experiments PDMA-18, PDMA-19, and PDMA-20 were designed to test process robustness by increasing monomer loading from 15% to 25%. In addition to the increased loading in the experiment PDMA-18, the monomer was injected to the reactor instantaneously, within a second. The bimodal chromatogram and high polydispersity (4.08) were caused by the highly exothermic reaction. Bubbles were observed in the reactor during the addition of monomer. The high reactor loading and fast monomer addition rate generated heat, increased reaction temperature, and gave bimodal distribution as shown in Figure 3.7.

SampleName	PDMA-18	Sample Type	Broad Unknown
Vial	20	Date Acquired	1/11/2002 2:00:21 PM
Injection	1	Acq Method Set	GPC
Injection Volume	150.00 ul	Processing Method	5367
Channel	410	Date Processed	1/14/2002 9:16:47 AM
Run Time	60.0 Minutes		

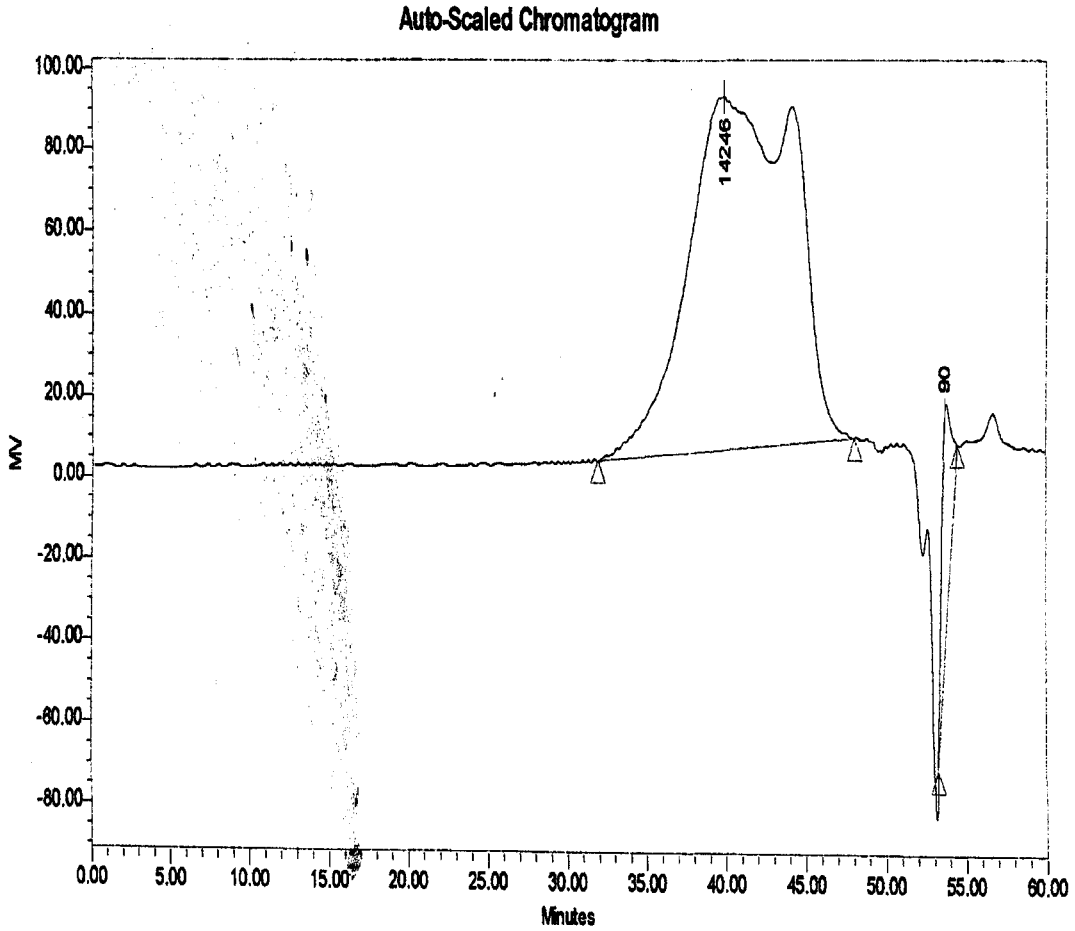


Figure 3.7 PDMA-18 GPC chromatogram

Retaining the monomer addition rate at 0.2 g/minute allowed for good heat dissipation and produced a controllable process as shown in the experiments PDMA-19 and PDMA-20. The molar ratio of triethylborane coordinating agent to the initiator was two-to-one.

The GPC in THF measurements consistently gave lower Mn than the calculated. Kobayashi and Okuyama [42] suggested that poly(dimethylacrylamide) chain has an expanded chain structure in DMF and contracted one in THF. The consistency of the GPC in THF measurements seems to be in agreement with this statement.

This consistency led to the statistical analysis of GPC in THF to adjust the measured Mn of the polymers with theoretical values. As it will be referenced in chapter 4, the actual Mn values will be used in the kinetic experiments.

The statistical analysis performed on the data set are presented in Table 3.11.

Table 3.11 Statistical analysis of Mn for poly(dimethylacrylamide) GPC in THF.

Statistical analysis of Mn

Experiment #	Theoretical Mn	GPC/THF Mn	GPC/Theoretical Mn
PDMA-8	6,000	4,925	0.82
PDMA-9	6,200	4,430	0.71
PDMA-10	6,130	4,490	0.73
PDMA-11	6,190	4,730	0.76
PDMA-12	6,470	5,060	0.78
PDMA-18	5,980	4,762	0.80
PDMA-19	6,330	4,730	0.75
PDMA-20	5,900	4,480	0.76

GPC/Theoretical Mn ratio	**0.76**
Standard deviation	**0.035**

This statistical analysis indicates that the macromonomer number-average molecular weight measured by the GPC in THF is 24% lower than the theoretical value.

Only the soluble in THF polymer samples with low polydispersity were used in the determination of the conversion factor for the actual size of the polymer. This conversion was a necessary step in the research study, because only the GPC in THF was available at most of the time, the experiments were performed.

Alternative GPC measurements were completed at McMaster University with dimethylformamide (DMF) and 0.01 molar lithiumbromide (LiBr) as eluent. In house reconditioned UltraSTYRAGEL columns were used as described early in this section. The polymer samples were marked with one drop of toluene each as a reference. This marking is a standard procedure used at Xerox Research Center, where the GPC measurements were done. The toluene peak serves as a reference. Similar marking was done with the GPC in THF measurements.

The extracted data presented in Table 3.12 indicate that the macromonomer Mn's exceeds the theoretical values. The polymer produced in the experiment PDMA-8 had Mn equal to 10120 g/mol compared to the theoretical 6000 g/mol. Eliminating the instrument defect and bringing base line stability did not give the expected result. The number-average molecular weight of the PDMA-8 was still higher than the theoretical Mn (9340 g/mol).

Table3.12 GPC analyses in THF and DMF

Experiment number	Theoret. Mn	Mn (THF)	PD (THF)	Mn (DMF) 1 run	PD (DMF) 1 run	Mn (DMF) 2 run	PD (DMF) 2 run
PDMA-8	6000	4925	1.20	10120	1.25	9340	1.57
PDMA-12	6470	5060	1.29	6680	1.62	8430	1.77
PDMA-13	6130	-	-	5970	1.21	6820	1.76
PDMA-20	5900	4480	1.13	-	-	6860	1.68

Run 1 GPC in DMF instability in base line, pressure differences during the runs, drop of toluene added as a marker, PMMA standards

Run 2 GPC in DMF base line stabilized, drop of toluene added as a marker, PMMA standards

Figure 3.8 and Figure 3.9 show GPC chromatograms of PDMA-8 with unstable and stable base line.

SampleName	8	Sample Type	Broad Unknown
Vial	109	Date Acquired	29/03/2002 7:57:00 AM
Injection	1	Acq Method Set	pin
Injection Volume	100.00 ul	Processing Method	PMMA INDMF MAR29
Channel	410	Date Processed	29/03/2002 7:43:38 PM
Run Time	40.0 Minutes		

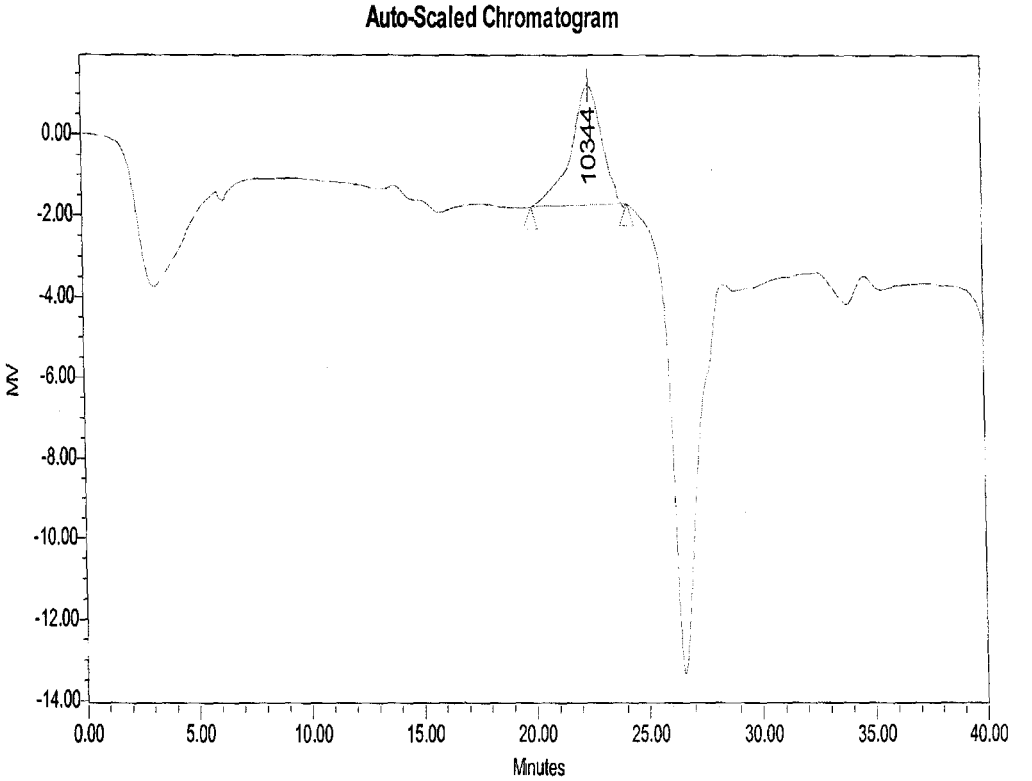


Figure 3.8 GPC in DMF – instability of the base line

SampleName	8	Sample Type	Broad Unknown
Vial	109	Date Acquired	03/04/2002 11:01:48 PM
Injection	1	Acq Method Set	pin
Injection Volume	100.00 ul	Processing Method	PMMA IN DMF Apri3th
Channel	410	Date Processed	04/04/2002 7:03:16 PM
Run Time	45.0 Minutes		

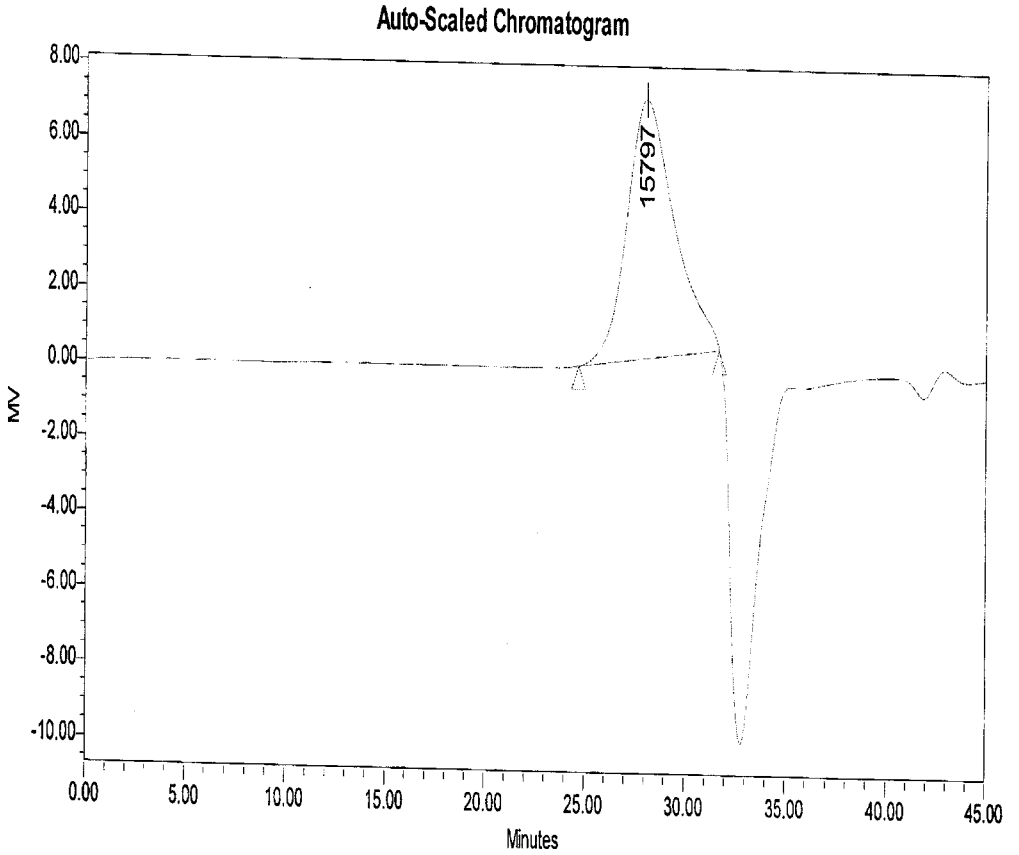


Figure 3.9 GPC in DMF – stability of the base line

The different GPC results were obtained when the polymer samples did not contain toluene as a marker. From the previous GPC chromatograms it was evident that the toluene peak affected the lower molecular weight region of the chromatogram. The GPC in DMF marked as Run 3 are shown in Table 3.13.

Table 3.13 GPC analyses in DMF

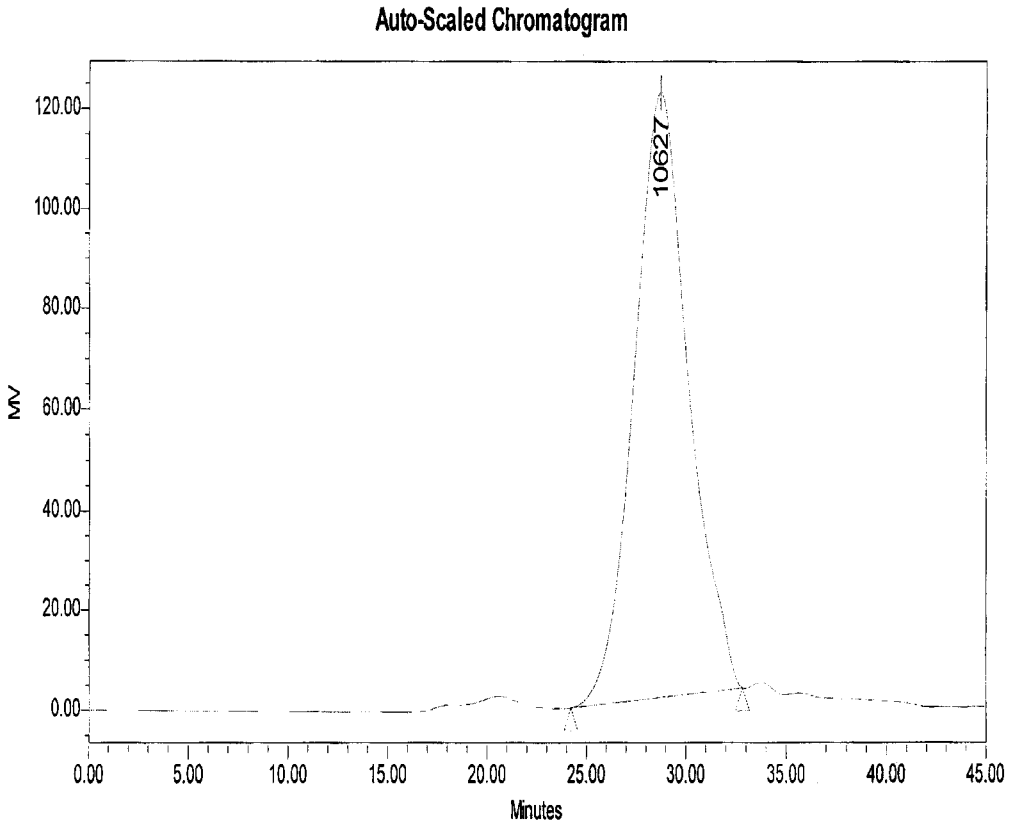
Experiment number	Theoretical GPC	GPC (THF)	Polydispersity PD (THF)	GPC (DMF) 3 run	PD (DMF) 3 run
PDMA-12	6470	5060	1.29	6400	1.84
PDMA-13	5600	-	-	5560	1.82
PDMA-20-4%	5900	4480	1.13	5690	1.80

Run 3 GPC in DMF base line stabilized, no addition of of toluene as a marker, PMMA standards

These results reflected the most accurate measurement conditions. The macromonomer should be analysed by using DMF and 0.01 molar LiBr solution as an eluent without any additional solvent marking. The number-average molecular weight of the polymer is in agreement with calculated Mn. The polymer of the theoretical Mn 6470 g/mol was measured as Mn 6400 g/mol (PDMA-12).

The PDMA-12 eluogram is shown in Figure 3.10.

SampleName	12r	Sample Type	Broad Unknown
Vial	46	Date Acquired	03/04/2002 2:59:33 PM
Injection	1	Acq Method Set	pin
Injection Volume	100.00 ul	Processing Method	PMMA IN DMF Apri3th
Channel	410	Date Processed	03/04/2002 6:00:39 PM
Run Time	45.0 Minutes		



Mn=6400 g/mol. Mw=11875 g/mol, PD=1.84

Figure 3.10 GPC PDMA-12

Noticeably high polydispersities in all the GPC in DMF measurements can be attributed to the quality of available UltraSTYRAGEL columns and associated "band broadening" issues. It was mentioned previously that they were extensively used and reconditioned.

There are four possible processes associated with band broadening in SEC:[56]

- eddy diffusion
- resistance of solute to mobile phase mass transfer
- resistance of solute to stationary phase mass transfer
- longitudinal diffusion

The eddy diffusion is caused by different paths the solute molecules take in the packed column around the packing beads. Some of the corridors are narrower than the others in the packing. It varies the velocity with which sample molecules move through the column. As a result, the elution band becomes broader.

The band broadening is caused by the resistance of solute to mobile phase mass transfer and is associated with the velocity gradient profile in a single flow stream. Molecules in the center of the flow stream move faster than those at the surface of column. The resistance of solute to stationary phase mass transfer is the most important factor in band broadening for SEC. It is caused by slow solute diffusions in and out of the pores of packing material. Large solute molecules with low diffusion coefficients will give a large band broadening. Some molecules diffuse into the pores, some move farther downstream. The longitudinal diffusion has minor effect on band broadening because of the slow diffusion along the column axis parallel to the flow direction.

Most probably, the resistance of solute to stationary phase mass transfer process is responsible for polydispersity of PDMA samples measured in DMF/LiBr in a range of 1.5 to 1.85. The solute in columns is retained unevenly due to inhomogenity in gel packing caused by the condition of these columns. The capability of size exclusion is limited with these columns as shown by the toluene (marker) peak at vicinity of the low molecular weight chromatogram tail (Figure 3.9).

Table 3.14 shows GPC measurements of two different samples varying in concentrations (0.3 wt% and 4 wt%). The molecular weight measurement of were done

in DMF and in THF eluents. In Runs 2, 3, and 4 DMF was a mobile phase with PMMA standards. In Run 5, THF was chosen as a mobile phase with PMMA standards.

Table 3.14

GPC analyses in DMF (variation in solute concentration)

Experiment number	Theoret. GPC	Mn DMF 2 run	PD DMF 2 run	Mn DMF 3 run	PD DMF 3 run	Mn DMF 4 run	PD DMF 4 run	Mn THF 5 run	PD THF 5 run
PDMA-20-0.3%	5900	6860	1.68	5690	1.80				
PDMA-20-4%	5900					5690	1.38	3825	1.25

Run 2 GPC in DMF, base line stabilized, drop of toluene added as a marker, PMMA standards
Run 3 GPC in DMF base line stabilized, no addition of toluene as a marker, PMMA standards
Run 4 GPC in DMF instability in base line, pressure differences during the runs, no addition of toluene as a marker, PMMA standards
Run 5 GPC in THF, PMMA standards, base line stable

The values in the last column indicate that the macromonomer Mn measured in THF with PMMA standards, is even more suppressed than the results obtained from the GPC in THF with polystyrene standards (Table 3.10).

3.6.2 Summary of GPC measurements

The measurements of the macromonomer molecular weight and polydispersity by GPC presented in section 3.6 indicate that the anionic synthesis of the PDMA macromonomer were controllable. The theoretical number-average molecular weights, Mn, were in the agreement with the measured value of the Mn. The polydispersity reflected the characteristic polymer chain distribution.

In the search for the most accurate GPC measurement system, the GPC analyses were done first in THF as a mobile phase with polystyrene standards. These

measurements gave consistent and lower than calculated values for Mn and low polydispersity. It was found that the macromonomer coils have a shrunk structure in THF by 25-30%.

DMF with 0.01 molar LiBr was used as an alternative mobile phase in the GPC measurements. The measured Mn values were in agreement with the theoretical Mns. This shows that the DMF is a better solvent for poly(dimethylacrylamide) macromonomer than THF.

Toluene used as a marker in GPC samples (standard Xerox procedure) had an adverse effect on the GPC in DMF measurements. The lower molecular weight region of the eluogram was affected by the toluene signal. It cut off the low molecular region resulting in higher than calculated molecular weight values. Removing toluene from samples and performing GPC analyses in DMF/LiBr gave the best conditions for the GPC system to be used in the macromonomer molecular weight measurements.

The high polydispersity measured in DMF was influenced by the poor quality of the GPC UltraSTYRAGEL columns. The polymer and toluene peaks were not well resolved and affected the measurements. The resistance of solute to the stationary phase mass transfer process was responsible for high polydispersity of these macromonomer samples. The solute in columns was most likely retained unevenly due to the inhomogenity in gel packing caused by the condition of these columns.

Polymethylmethacrylate (PMMA) standards gave better results than polystyrene standards in DMF measurements. The PMMA is closer to the studied macromonomer in terms of the chemical structure, since both of them belong to alkyl methacrylates group.

The base line stability in the GPC measurements is an important factor in determining the actual polymer Mn. Solvents used as a mobile phase have different viscosities and the GPC instrumentation must be adjusted to incorporate these viscosity differences. It affects the base line stability.

The GPC study allowed to select the best measurement conditions for poly(dimethylacrylamide) macromonomer. Based on all measurements performed at different conditions in terms of solvent type, sample concentration, and standards, DMF with 0.01 molar LiBr at 4% wt polymer concentration, and PMMA standards are the optimal settings for this macromonomer measurements. The column condition is critical in determining polydispersity. Band broadening caused by the column residue from the previous usage increases the macromonomer polydispersity.

3.7 Polymer characterization by NMR measurements

3.7.1 Experimental work – ^{1}H NMR measurements

A Fourier transform spectrometer was used in this research study. The spectrometer specifications are shown in Table 3.15.

Table 3.15 XRCC NMR spectrometer technical data

Bruker Avance DPX 300 NMR Spectrometer
- 7.0 T magnet
- 300 MHz ^{1}H Frequency
- Broadband X-Transmitter; 4-Nucleus Probe (2 Channel System; ^{1}H, ^{13}C, ^{19}F, ^{29}Si)
- 5mm probe
- Software: Bruker NMR Suite version 2.6, used with a PC.

The samples were prepared in deuterated chloroform for both ^{1}H NMR and ^{13}C NMR.

The NMR analyses were done at McMaster University and at XRCC. Both, proton ^{1}H NMR and carbon ^{13}C NMR measurements were carried out on a number of polymer samples. The purpose of ^{1}H NMR was to:

- determine the structure of macromonomer

- determine the yield of the macromonomer
- measure Mn

The purpose of ^{13}C NMR was to:

- determine the tacticity of polymer (ligand to initiator ratio varied)
- quantify the tacticity (number of scans increased, delay acquisition time changed)

The polymer structure was determined based on available references.[33,41,42] Figures 3.11 and 3.12 represent ^{1}H NMR spectra of PDMA-21-a and PDMA-21-i samples.

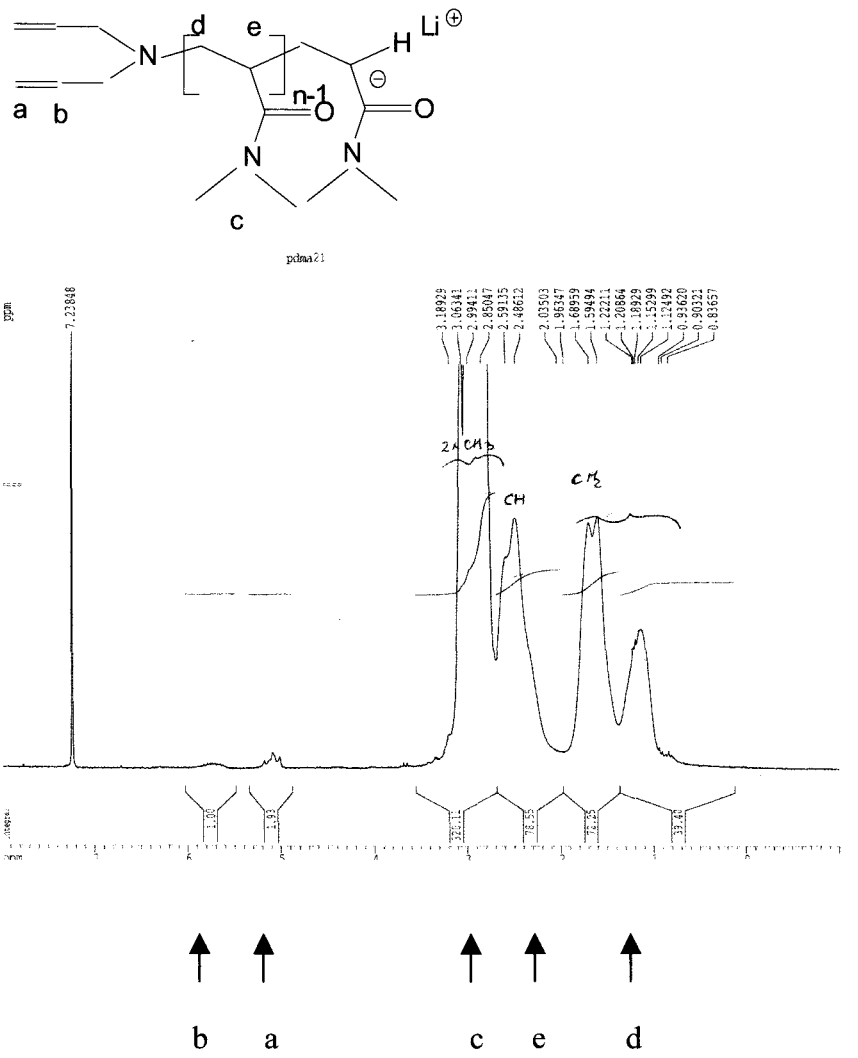


Figure 3.11 ^{1}H NMR spectrum of PDMA-21-a (soluble in THF)

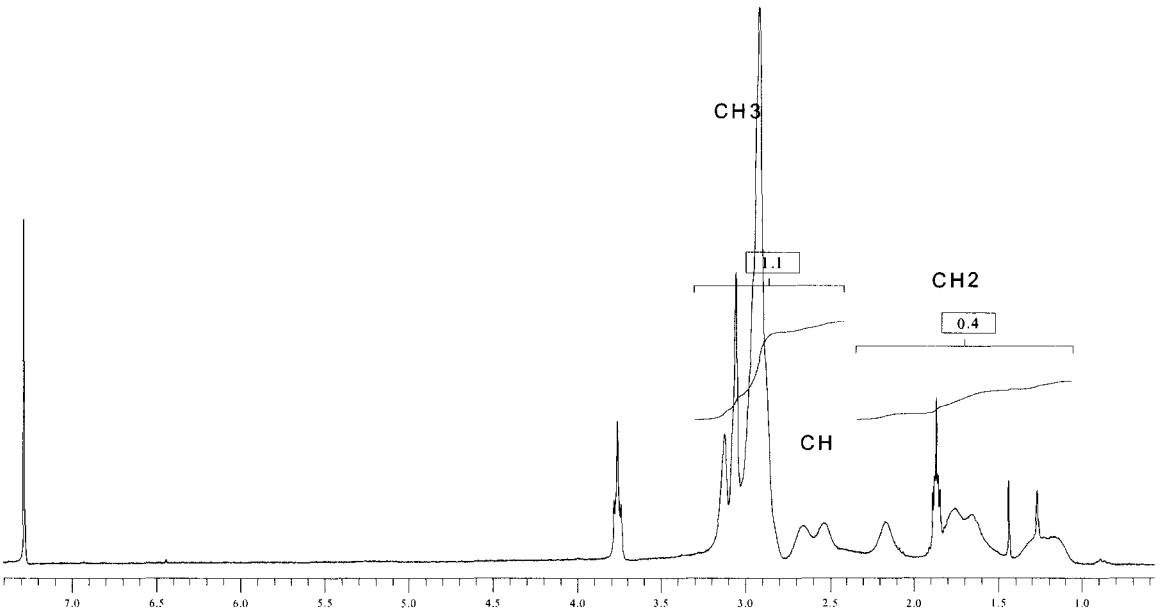


Figure3.12 ^{1}H NMR spectrum of PDMA-21-i (insoluble in THF)

These two ^{1}H NMR spectra were prepared at McMaster University (PDMA-21-a) and at XRCC (PDMA-21-i). They represent the polymer produced in one experiment (PDMA-21). This polymer was synthesized without any coordinating agent. After the addition of monomer, an insoluble product was synthesized within few seconds after the monomer injection. The solid was removed from the reactor and the liquid was transferred to hexane. The solid was dried and analyzed by NMR as PDMA-21-i (isotactic, insoluble in THF).

A small fraction of the soluble polymer was precipitated in hexane and dried in an oven. This sample was analyzed by NMR as PDMA-21-a (atictic, soluble in THF).

There is an evident difference in the structure of the polymer. The peaks are not well resolved, especially in case of the PDMA-21-i spectrum.

The type of samples analyzed by NMR will have an influence on the signal produced. Low molecular weight samples will have narrow signal peaks. High viscosity polymer solutions will have broader line widths due to limited motion of polymer

chains.[58] As a viscous polymer in solution, the PDMA-21-i had broader line widths due to limited motion of polymer chains.

The PDMA-21-a spectrum has the characteristic resonances for $N(CH_3)_2$ at 2.8-3.2 ppm, for CH at 2.3-2.7 ppm, and for CH_2 protons at 1.2 -1.7 ppm. Integrating the peaks of $N(CH_3)_2$ together with CH gives the value of 398.77 (320.11+78.55=398.77).

Integrating the peak of CH_2 gives the value of 111.65 (72.25+39.40). Similar results were obtained by Xie.[33] Due to the poor resolution of CH and CH_3 signals, they were combined into one integral. The values obtained from integration can be used to verify the macromonomer structure and assign peaks to the particular protons. This peak assignment is based on the following calculations:

$N(CH_3)_2$ + CH	= 398.77	398.77 / 7 protons = 57
CH_2	= 111.65	111.65 / 2 protons = 56

These numbers indicate the correct peak assignment and show that each macromonomer chain consists of 57 monomer units. The one monomer unit difference is attributed to the measurement error.

As indicated by Kobayaschi [42] NMR is one possible method for determining stereoregularity of the polymers. This aspect of the characterization will be discussed in section 3.7.2.

The ^{1}H NMR spectrum of the isotactic polymer reveals more signals than that of atactic, soluble-in-THF, polymer. The integrations of the peaks are not in stoichiometric agreement since the integrals from CH_2 protons (0.4/2 protons = 0.2) and from CH and CH_3 combined (1.1/7protons = 0.16) are not equal to each other. The isotactic polymer in the form of physical gel formed immediately after the monomer addition and most likely entrapped THF solvent in its structure. Referenced ^{1}H NMR spectra of THF and *N,N*-dimethylacrylamide monomer show this possibility. [60]

The second objective of the NMR measurements was to determine the survived fraction of terminal chain end double bond. Since diallylamine is a part of the polymer structure, it could be used as a reference. The ^{1}H NMR signals for diallylamine show peaks at 5-5.2 ppm (CH_2) and 5.6-5.9 ppm (CH).[24] The relative strength of signals from the chain end and the protons from the polymer can give an indication of the fraction of the chain end double bond survived. The polymer Mn must be sufficiently low (up to 10000 g/mol) to have diallylamine proton signals accurately integratable.

A sample calculation is based on PDMA-21-a. The ^{1}H NMR spectrum of this macromonomer is shown in Figure 3.11. The macromonomer Mn was equal to 5900 g/mol. This is equivalent with 60 monomer units in a polymer chain. The signal integrations shown on the previous page gave 57 monomer units in the polymer chain. The measurement error can be attributed to this small difference in integration results. The diallylamine CH_2 integrated signal is equal to 1.93. This integral corresponds to 0.48 proton fraction (1.93 / 4 protons = 0.48, 2 CH_2 groups in one diallylamine molecule) from diallylamine CH_2 group for 57 protons from the polymer chain. Therefore, for one diallylamine molecule, there are 118 (57 / 0.48 = 118) monomer units. The surviving fraction of polymer chains with double bond is 0.51 (60 / 118 = 0.51). Therefore the ^{1}H NMR method shows that almost half of the double bond terminal groups originating from diallylamine were lost during the polymerization in PDMA-21 experiment.

The fraction of survived terminal double bond obtained from PDMA experiments and analyzed by the ^{1}H NMR are shown in Table 3.13.

Table 3.15 The fraction of survived terminal double bond

Experiment number	Yield determined from ^{1}H NMR [%]	Coordinating agent to initiator ratio	Experiment purpose
PDMA-10	91	2:1	Reproducibility

PDMA-11	75	2:1	Reproducibility
PDMA-19	50	2:1	Process conditions
PDMA-20	38	2:1	Process conditions
PDMA-12	86	1.5:1	Coordinating agent to initiator ratio
PDMA-15	87	1:1	Coordinating agent to initiator ratio
PDMA-17	Signal interference	0.5:1	Coordinating agent to initiator ratio
PDMA-21 (atactic)	51	0:1	Coordinating agent to initiator ratio
PDMA-21 (isotactic)	35	0:1	Coordinating agent to initiator ratio

Reproducibility - repeated experiments at identical conditions

Process conditions – monomer addition 15 minutes after Et3B injection (60 minutes standard procedure)

Coordinating agent to initiator ratio – variation in ligand concentration

The macromonomer yield determination by ^{1}H NMR indicates that the activity of double bond functional group from diallylamine is preserved. This is a critical variable in utilizing the macromonomer in further polymerization. The macromonomer yield varied. The highest values were achieved in experiments with high ratios of the coordinating agent to initiator. The experiments PDMA-10 and PDMA-11, where ligand concentration was in excess of two to one, gave 91% and 75% yields respectively. Lower fractions of survived double bonds were obtained from PDMA-19 (50%), PDMA-20 (38%), and PDMA-21 (51% atactic soluble in THF fraction, 35% insoluble in THF fraction). These three experiments were run at slightly changed process conditions. As a standard procedure, the monomer was added after one hour from the addition of coordinating agent. For PDMA-19, PDMA-20, and PDMA-21, the monomer was added ten minutes after the introduction of coordinating agent to the reactor.

The goal of varying the addition time of monomer to reactor was to investigate if the initiator system is terminated when allowing one hour of time to pass and also to see if there is time required to build the initiator system and stable complexes with coordinating agent. High values of number-average molecular weight, would be observed if the termination had occurred. This did not happen.

The decreased macromonomer fraction of survived polymer chain end double bond in these three experiments indicates that there was no sufficient time to establish a stable initiator system consisting of diallylamine and *sec*-butyllithium and to have stable coordinating complexes. The high fractions of survived chain end double bond were achieved with ligand in excess of one-to-one molar ratio over initiator as shown in PDMA-12 and PDMA-15 experiments. Yields were equal to 86% and 87% respectively.

The low survival rate was observed with no coordinating agent present. The atactic fraction (soluble in THF) of the product of PDMA-21 gave 51% yield and isotactic fraction only 35%.

The results from the PDMA experiments show that the macromonomer can be synthesized with the presence of coordinating agent. At least one hour is needed for the reaction of diallylamine bearing an end functional group of the macromonomer with initiator before monomer is added.

An alternative approach to measure the macromonomer Mn by ^{1}H NMR was considered due to the low molecular weight of the synthesized polymer. This approach was based on a similar principle to the determination of the macromonomer yield. If all diallylamine molecules were incorporated into the Poly(dimethylacrylamide), the polymer Mn could have been determined as the ratio of the polymer proton integrated signal to the integrated double bond end functional group CH or CH_2 signal. Due to the reduced macromonomer yield, this approach was not accurate and was rejected. The GPC method described in section 3.6 was used instead.

3.7.2 Experimental work - ^{13}C NMR

In contrast to ^{1}H NMR, which has small chemical shift range of 10 ppm, ^{13}C NMR has a broad range of 250 ppm. ^{13}C NMR has low sensitivity and has 1/5700 strength of ^{1}H NMR.[58] ^{13}C nucleus is sensitive to small changes in the immediate electronic environment and can be successfully used in polymer stereoregularity investigations. A number of macromonomer samples were analyzed by ^{13}C NMR to determine the stereoregularity of product. These measurements were done with a varying number of scans, ns, to produce the best spectrum quality. To increase signal to noise ratio, a number of pulses is increased. Random noise will add as a square root of the number of scans, whereas NMR signal will add by summation of number of scans.[61]

The default settings of 1024 was changed to 4096, and 20000. The highest signal to noise ratio was achieved with 20000 scans and 1.37 seconds pulse delay for each acquisition. The run with such a high ns was done after 13 hours and 18 minutes. The ^{13}C NMR of PDMA-21 is shown in Figure 3.13

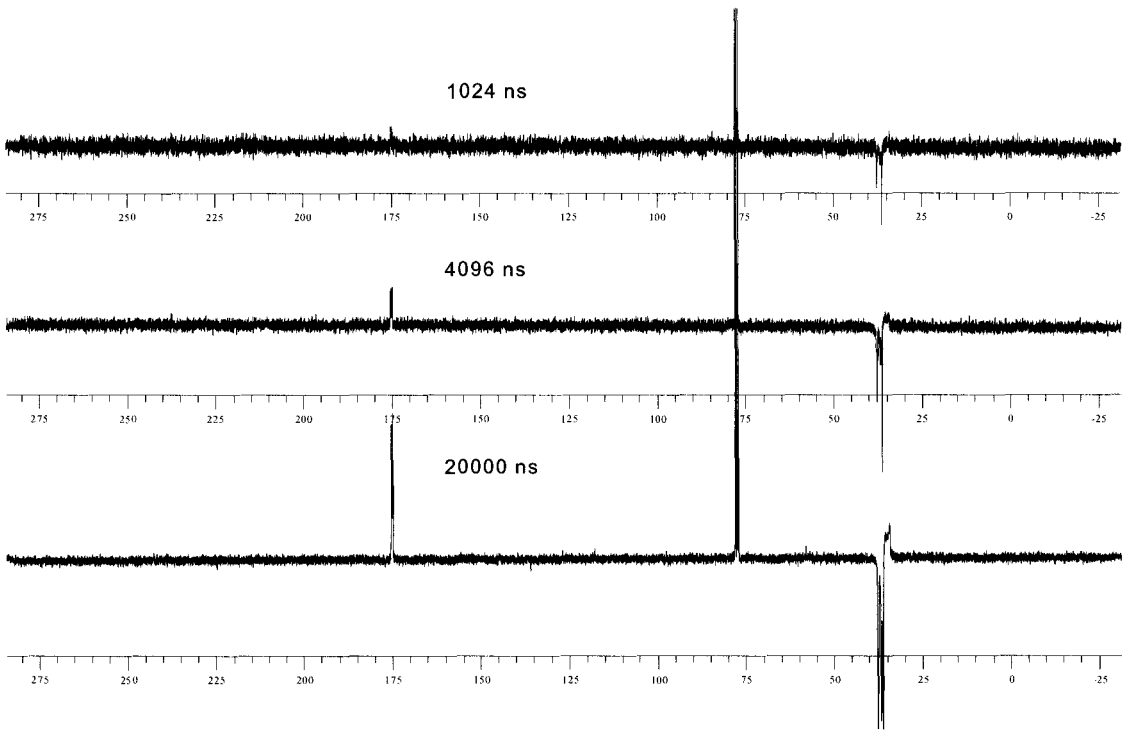


Figure 3.13

^{13}C NMR spectrum of PDMA-21-a

These three spectra show that 20000 scans for each analysis has the best signal to noise ratio. Therefore 20000 scans was set for each ^{13}C NMR analysis. In the experiment with 1024 scans (default settings), the signal of interest at 175 ppm is hardly visible. The sample concentrations were the same in each measurement and were prepared as 20 mg of the polymer in 1 ml of chloroform-d. The higher concentration samples were very viscous. The characteristic signals for PDMA are at 37.645, 37.512, 36.706, then 36.194 ppm, 34.221 ppm, and 174.725 to175.158 ppm. The signal of interest is the downfield signal (the least shielded nucleus) in the neighborhood of 175 ppm region. Both, soluble and insoluble products were analyzed. The polymers with all studied coordinating agent to initiator ratios were measured for ^{13}C NMR.

The objectives of this study were to determine stereoregularity of macromonomer and to quantify racemic and meso structures of the analyzed materials. Racemic r dyads are pairs of adjacent asymmetric centers with the opposite optical configuration. Meso m dyads have the same optical configuration. The former is syndiotactic, the latter is isotactic.

In order to attempt to quantify the isotactic, syndiotactic and atactic structure, the interval between NMR pulses must be sufficiently high to allow the system return to equilibrium.[58] Figure 3.14 shows two ^{13}C NMR spectra from the PDMA-21 experiment, one with the default pulse delay PD 1.37 seconds, the other with PD 2.8 seconds.

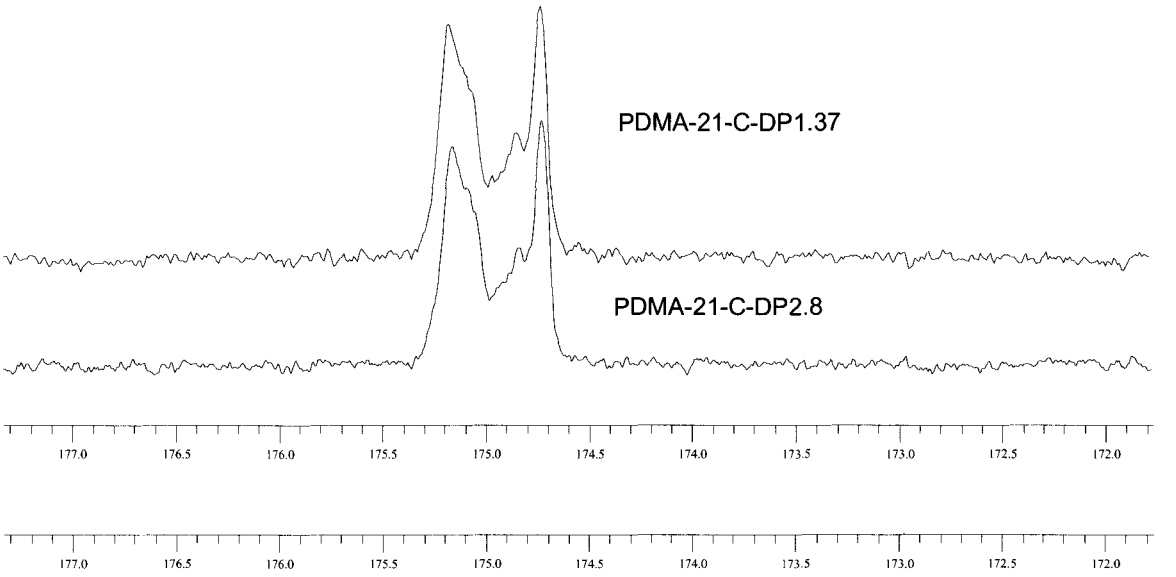


Figure 3.14 ^{13}C NMR spectra of PDMA-21-a with different pulse delays PD

This analysis with the varying pulse delays indicates that the default setting for pulse delay 1.37 seconds allows for the sufficient relaxation time for the system return to equilibrium. Based on this analysis, all remaining ^{13}C NMR spectra were done with PD 1.37 seconds.

A sample ^{13}C NMR spectrum is shown in Figure 3.15. Figure 3.16 represents a magnified part of the same polymer spectrum at 175 ppm.

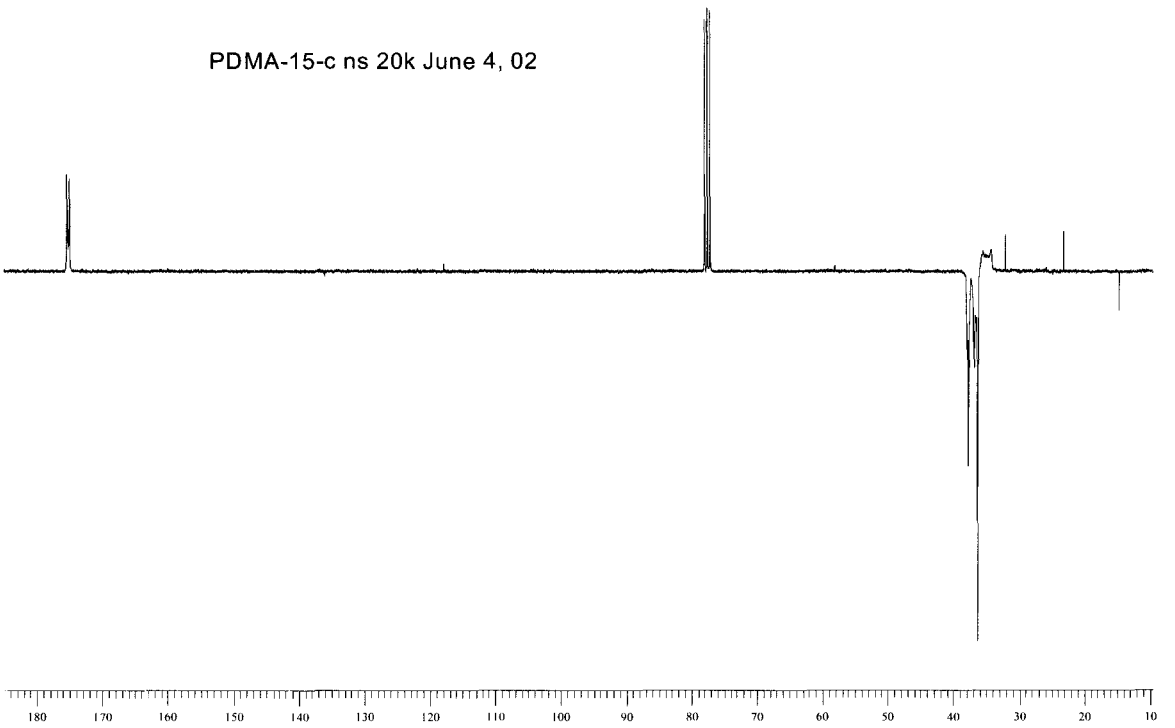


Figure 3.15 ^{13}C NMR spectrum of PDMA-15

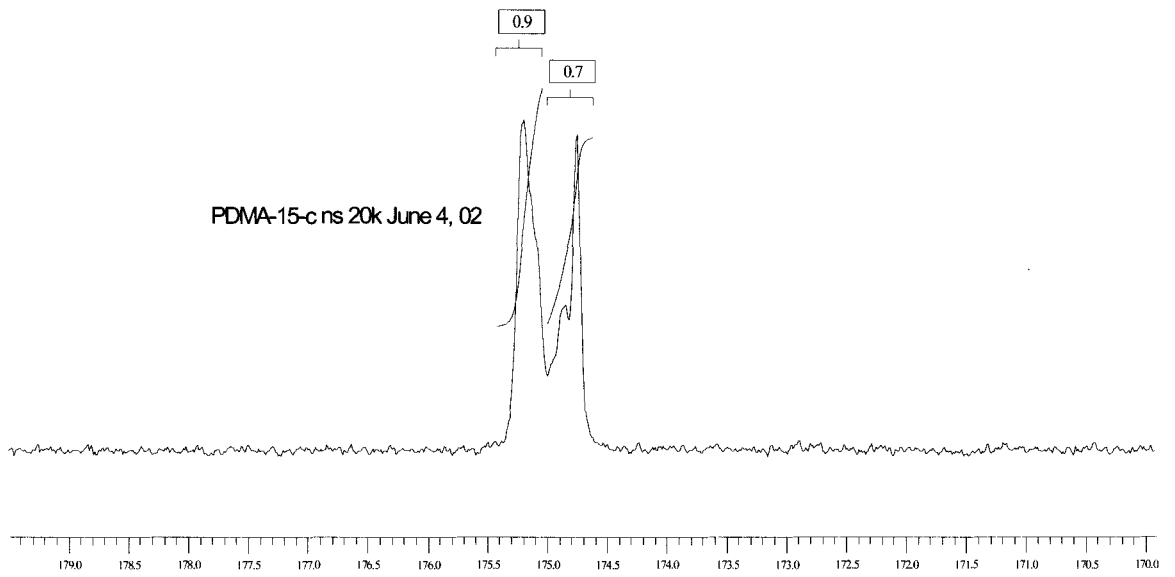


Figure 3.16 ^{13}C NMR spectrum of PDMA-15 (magnified)

The signal at 175.74 corresponds to rr (syndiotactic) and at 174.18 ppm to mm (isotactic) polymer. The small signal at 174.88 ppm may indicate mr heterotactic structure, in which there are triads within the pentads with rr structure. As the magnetic field strength increases, the number of signals from CH groups increases because the resolution improves. All the signals can therefore be identified as pentad sequences. Instead of three adjacent monomer units, five adjacent monomers can give signals on the NMR spectrum with the high magnetic field strength. This analysis becomes very complicated. It is based on Markov statistics. Additional signals, which are not well resolved, give information about pentad structures (mmmm, mmmr, rmmr, mmrm, mmrr, rmrm, rmrr, mrrm, rrrm, rrrr).[61]

For the purpose of this research study, triads are discussed. The absorption at 174.6 ppm to 175.0 ppm will be attributed to isotactic polymer and the signal at 175.0 ppm to 175.4 ppm to the syndiotactic polymer. Absorption at 175.0 ppm will correspond to a solubility cutoff line. The integrated signal below 175.0 ppm will be attributed to insoluble polymer in THF and that of 175.0 ppm and up to the soluble polymer.

All the ^{13}C NMR spectra show characteristic signals in the 175 ppm region and are similar to Kobayashi [40,42] and Xie [33] with a difference in signal shift for all the absorption regions by 0.5 ppm downfield.

The PDMA-15 ^{13}C NMR spectrum was centred in the 175 ppm region and integrated to determine the syndiotactic and isotactic with atactic fraction of the polymer. As shown in Figure 3.16, the PDMA-15 polymer has 44 % isotactic fraction and is not soluble in THF. The fraction of insoluble polymer was calculated as $\frac{0.7}{(0.7+0.9)} = 0.44$

The structure analyses of the macromonomer were done by ^{13}C NMR on a number of prepared samples with the coordination agent to initiator ratio varied from zero to two. ^{13}C NMR spectra for each experimental condition are overlaid in Figure 3.17.

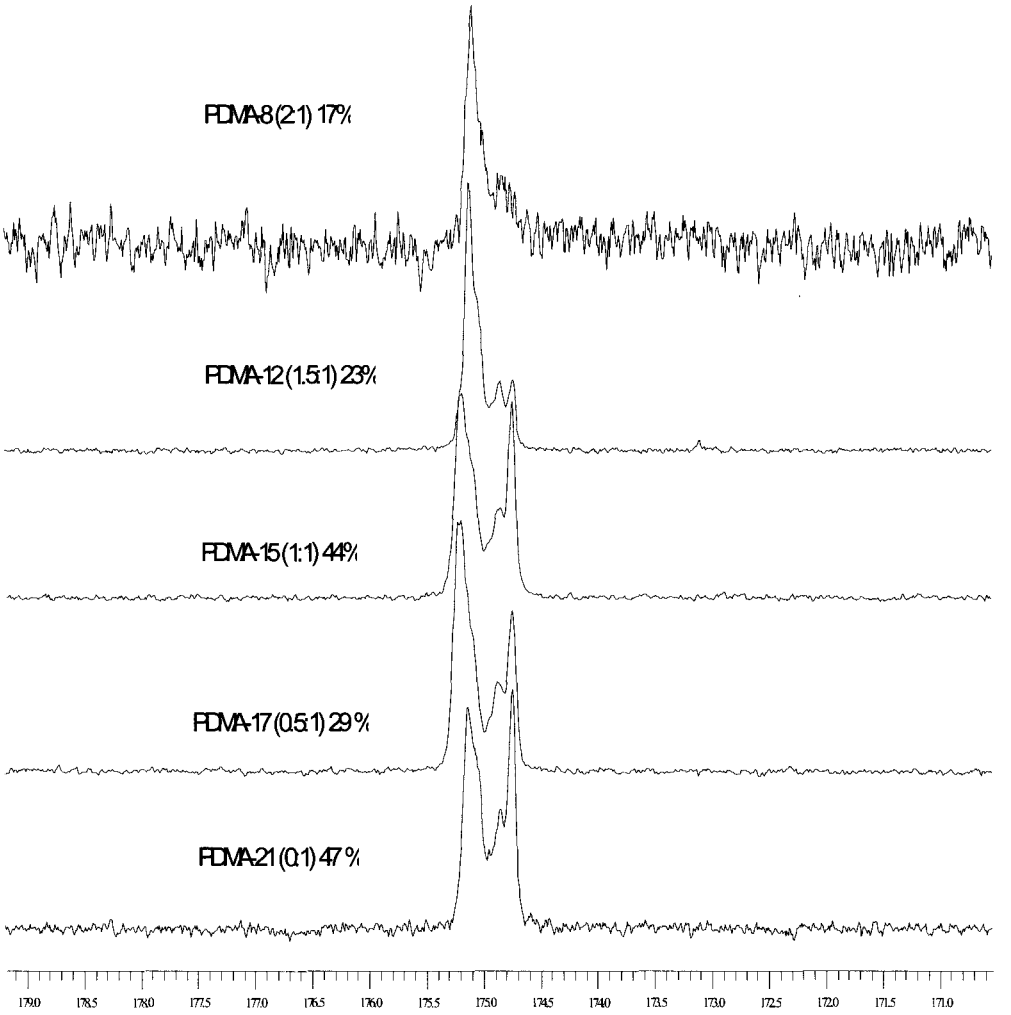


Figure 3.17 ^{13}C NMR spectra for tacticity determination

The highest isotactic fraction was found in the experiment PDMA-21, in which no coordinating agent was used. It reached 47 %. The polymer was not soluble in the reaction solvent and precipitated shortly after the monomer addition. By adding triethylborane to the reaction in 0.5 molar ratio to initiator, the isotactic content of the product decreased to 29 %. A significant decrease of isotacticity was observed in the PDMA-12 experiment. The coordinating agent to initiator ratio was equal to one and a half to one. Only 23% of the polymer was isotactic. The product was soluble in THF.

A further decrease of isotacticity was noticed on the PDMA-8 spectrum. In this experiment, the ratio of triethylborane to *sec*-butyllithium was held as two to one and the polymer was soluble in the reaction solvent.

3.7.3 Summary of NMR measurements

The NMR measurements presented in section 3.7 show that both ^{1}H NMR and ^{13}C NMR were very powerful in characterizing the PDMA macromonomer. This technique was useful in determining the structure and yield of the PDMA and allowed to determine and quantify the polymer tacticity.

The fraction of survived chain end double bond of the macromonomer varied and depended on the concentration of coordinating agent used in the reaction. Over one and a half molar excess of triethylborane to initiator gave over 75% polymer with chain end functional group. Low survival rates obtained from the experiments without coordinating agent could be attributed to the termination of the double bond from diallylamine. The termination was likely caused by the fast reaction rate. The addition of triethylborane to slowed down the propagation and separated counterions with a sufficient distance to give soluble-in-THF polymer. The highest yields were obtained at two-to-one ratio of the coordinating agent to initiator.

A time period in proximity of one hour was required to allow for the initiator system to be synthesized, to effectively incorporate the chain end functional group. The monomer addition shortly after the coordinating agent injection did not allow the system establish equilibrium. This fast addition of the monomer decreased the macromonomer yield.

Both factors, the concentration of coordinating agent and the time required for the initiator system to equilibrate with triethylborane will determined the macromonomer yield.

Although the degree of polymerization of the macromonomer was low (60 monomer units in a polymer chain), it did not allow for the determination of the number-average molecular weight by the NMR. The instability of the macromonomer yield eliminated this method from the analysis.

The ^{13}C NMR measurements were time consuming. Each analysis required over 13 hours. It was necessary to obtain a high signal to noise ratio because the NMR signal of interest at 175 ppm had a low intensity.

Increasing the signal to noise ratio and testing the relaxation times by varying the pulse delay allowed for the quantitative approach to determine the macromonomer tacticity and interrelated solubility in THF. The borderline shift at 175.0 ppm was established as the solubility cut off line. The NMR signals were not well resolved in this spectrum region indicating the presence of atactic polymer between syndiotactic and isotactic chains. It was found that the isotactic fraction of macromonomer below 23 % gave solubility of the polymer in THF. The concentration of coordinating agent must be at least one and a half of the initiator concentration to achieve complete polymer solubility. The lower concentration of the ligand (one to one or less) produced an isotactic insoluble-in-THF product. There was not enough ligand to sufficiently coordinate growing polymer chains to eliminate isotactic mode of the monomer addition. The control of the polymerization process became impossible at this low ligand concentration.

3.8 Optimal conditions for polymerization and characterization of poly(dimethylacrylamide) macromonomer

Anionic polymerization used to synthesize poly(dimethylacrylamide) macromonomer required an extensive effort to prepare the system free of impurities. The equipment was meticulously cleaned and the reagents with reaction solvent purified by long refluxing.

The small scale of experimentation called for an accurate weighing technique to have a good process control. The optimal experimental conditions gave controllable polymerization and produced macromonomer with well-defined structure.

The best results in terms of polymerization control were achieved under the following conditions:

- THF solvent, diallylamine, *sec*-butyllithiu initiator
- temperature of 0°C
- triethylborane coordinating agent with two-to-one ratio over the initiator
- 30 minutes reaction time
- 60 minutes for ligand reaction with initiator prior monomer addition
- mixing with a magnetic Teflon coated stirring bar

The molecular weight determination done by GPC at various conditions led to the selection of DMF with 0.01 molar LiBr as optimal mobile phase. Mn of macromonomer samples analysed in DMF were close to the theoretical values.

^{1}H NMR used in the characterization allowed for the macromonomer structure confirmation and the determination of chain end double bond fraction survived after the process termination. Only atactic and syndiotactic polymers could be correctly analyzed by ^{1}H NMR. A poor signal resolution of isotactic samples did not allow for structure analyses.

^{1}H NMR measurements also showed that the fraction of survived chain end double bond was affected by the monomer concentration and time intervals between coordinating agent and monomer additions. Lower monomer concentrations (~15%) and long waiting periods for establishing a stable initiator-coordinating agent complexes (~60 minutes) improved the chain end double bond survival rate.

^{13}C NMR measurements used in the stereoregularity quantification required long time since the signal of interest at 175 ppm had to be elevated by high number (20,000) of NMR scans (increased signal to noise ratio). Pulse delay was determined as 1.37 seconds for each scan. All NMR measurements were performed in deuterated chloroform.

CHAPTER 4

Kinetic studies of the macromonomer polymerization

4.1 Introduction

Kinetics provides information about reaction rates and gives insight into reaction mechanisms. It is another aspect of polymerization control. Kinetic measurements indicate conditions under which reactions can be operated. In commercial processes, the reaction conditions must be known in order to design proper reactors and to evaluate the feasibility of the process from an economic point of view.

This chapter of the thesis deals with kinetic measurements of poly(dimethylacrylamide) macromonomer conditions. A general approach was taken to determine the polymerization temperature, at which adequate time interval samples of the polymer could be taken from a batch system. Furthermore, the propagation rate constant could be determined and the livingness of the polymerization system investigated.

As presented in Section 2.3, Figure 2.10, the reaction mechanism for the macromonomer synthesis involves at least two propagating species with different propagation rate constants. The presence of triethylborane coordinating agent in the system controls the stereoregularity of the polymer. The absence or low concentration of this ligand gives isotactic product, insoluble in the reaction solvent, whereas doubling the concentration of treethylborane in relation to initiator decreases isotacticity and gives solubility of the material in THF. Two types of propagating centers are formed with different degrees of separation between anion and cation in the initiator system. Insufficiently separated counterions determine the mode of monomer addition leading to isotactic structure. Higher separation gives the second type of propagating center and produces soluble syndiotactic polymer. There exists an equilibrium between these two center types.

Kinetic measurements have to be conducted in a system that allows for sampling at predetermined time intervals. Depending on the duration of the reaction, three types of reactors can be used:[62]

- Flow tube
- Automatically controlled reaction vessel
- Conventional stirred batch reactor

A flow tube can be used for reactions with half lives of 0.05 seconds to 2 seconds. A half life of reaction is the time required for 50% monomer conversion. An automatically controlled reaction vessel is used for reactions with half lives of 2 seconds to 20 seconds and stirred reactors for reactions with half lives above 20 seconds.

The only available means in our labs to perform kinetic studies was a conventional stirred batch reactor, a round bottom, 50 ml glass flask with a magnetic stirring bar. Therefore, the study required a search for the reaction temperature that would give a half life of 20 seconds or more.

4.2 Experimental work and results

The experimental kinetic work was divided into two stages. The first stage included a set of anionic polymerization experiments to synthesize the macromonomer at different temperatures. The goal of this stage was to find the appropriate conditions to obtain four to six time interval samples during the propagation. These samples were analyzed by GPC for the molecular weight, Mn and polydispersity, PD.

The second stage of the kinetic study included the kinetic analysis of the selected experiment. This experiment was conducted at the –7°C.

Table 4.1 shows the set of kinetic experiments and polymerization temperatures. All these experiments were performed in THF with triethhylborane to initiator ratio two-to-one.

Table 4.1 Polymerization temperatures

Experiment number	Experiment temperature [°C]	Total reaction time [min]	Sampling time [min]
PDMA-25	-77	120	5, 45
PDMA-26	0	180	1, 5, 32, 92
PDMA-27	-10	230	0.5, 2
PDMA-28	-40	220	1.75, 5
PDMA-29	-7	30	3, 6, 14

All kinetic experiments were performed at the conditions described in section 3.2. Sampling was done by inserting a needle with a syringe into the reaction flask and removing 2 ml of the solution during the polymerization at the predetermined time intervals. Samples were prepared for GPC in THF measurements.

The PDMA-29 experiment was selected for detailed kinetic studies. It was performed in four reactors (glass round bottom flasks). Samples were taken after reaction termination and the polymer yield was determined gravimetrically.

The experiments performed at temperatures –77° and –40°C had very slow kinetics and failed to produce polymer peaks in the GPC chromatograms.

In the PDMA-28 experiment, the samples were taken at 1minute 45 seconds and at 5 minutes. The PDMA-25 samples were taken at 5 minutes and 45 minutes after monomer addition. The PDMA-28 reaction was terminated after almost four hours and the PDMA-25 after 2 hours. The sample GPC curve for PDMA-28 is shown in Figure 4.1.

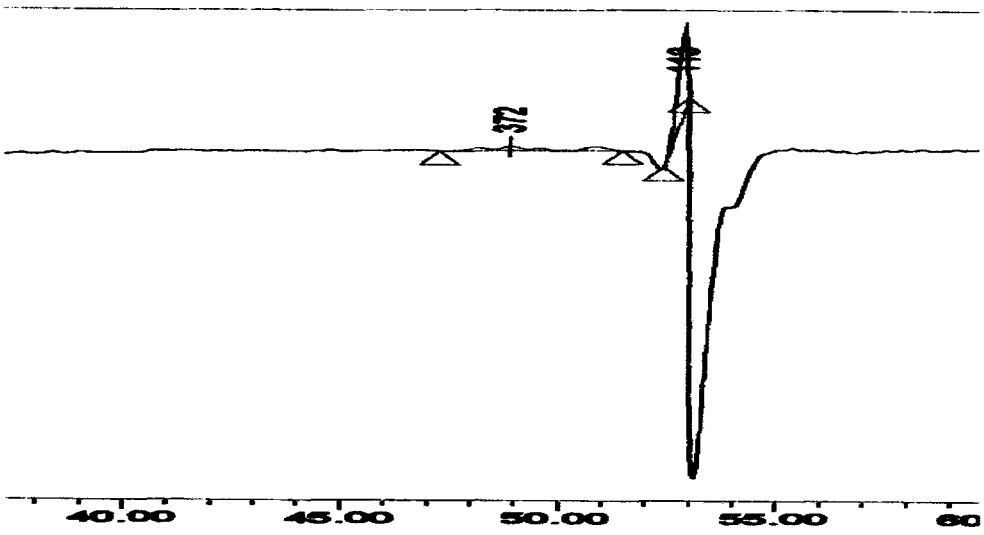


Figure 4.1 PDMA-28, 5 minute GPC in THF sample

The PDMA-26 experiment was performed at 0°C. Four samples were taken at 1, 5, 32, and 92 minutes. The GPC in THF run for each of these samples indicates that after 1 minute the Mn was equal to 6000 g/mol, after 5 minutes 6400 g/mol, after 32 minutes 7000 g/mol and after 92 minutes 7200 g/mol. This experiment indicated that 0°C is too high for kinetic studies since the one-minute sample had 83 % conversion.

The experiment performed at –10°C gave an indication of the correct temperature for a detailed kinetic study. The GPC in THF of two samples taken at 30 seconds and 2 minutes gave an Mn equal to 570 g/mol and 980 g/mol respectively, as shown in Figure 4.2 and 4.3.

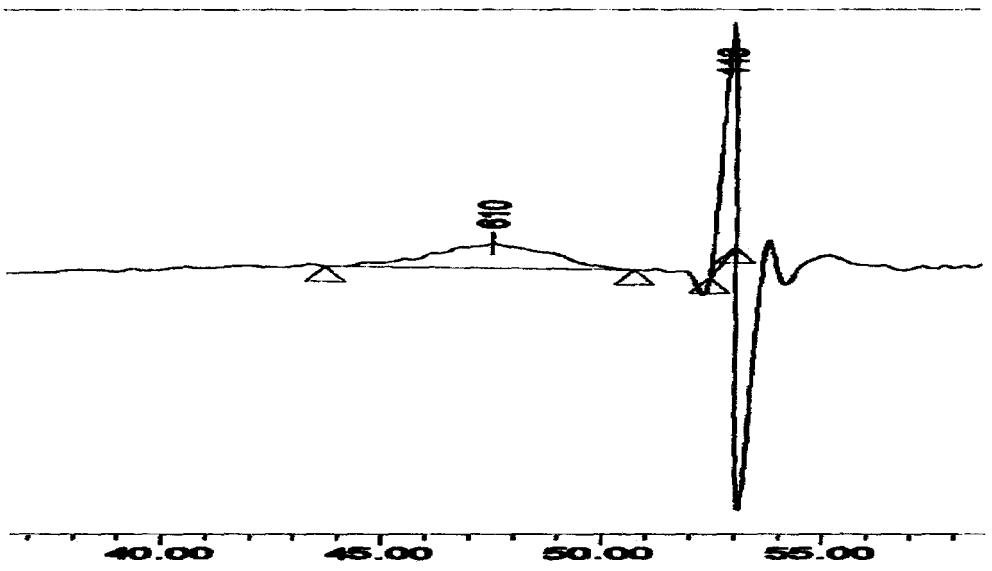


Figure 4.2 GPC/THF PDMA-27B (0.5 minute sample); Mn = 570, PD = 1.25

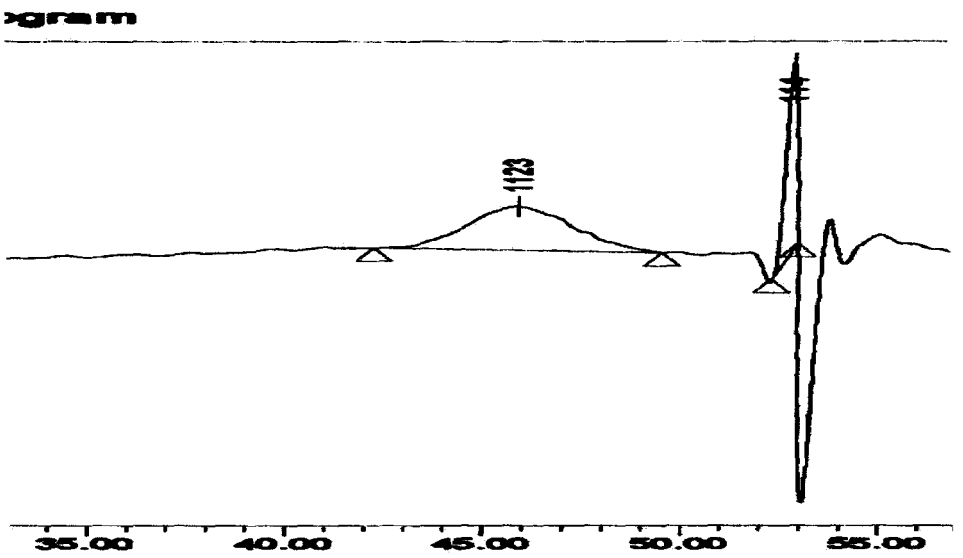


Figure 4.3 GPC/THF PDMA-27A (2 minute sample); Mn = 980, PD = 1.25

For the kinetic analysis of PDMA-29 performed at –7°C, the following data were obtained:

- concentration of living ends during reaction $[C^*]$
- conversion x
- number average degree of polymerization Dp
-

This experiment was performed at the following conditions:

- reaction time τ (30 minutes)
- initial monomer concentration $[M]_0$ (1.16 mol/l)
- initial initiator concentration $[I]_0$ (0.0173 mol/l)

Four samples were taken during the PDMA-29 polymerization, starting at 3, then 6, 14, and 30 minutes. The conversion x was determined by precipitating the polymer in hexane, drying it out in a vacuum oven, and weighing the dry polymer.

The concentration of living chain ends $[C^*]$ during reaction was determined from the fraction of monomer converted and the degree of polymerization Dp as shown in Equation 4.1.[62]

Equation 4.1 Concentration of living ends

$$[C^*] = k \cdot \frac{[M]_0 \cdot x}{D_p}$$

k is the number of living ends per polymer chain. For the polymer samples B, C, D, and E, the concentrations of living chain ends were equal to 0.017, 0.017, 0.020, and 0.018 mol/l, respectively.

The Mn was measured by GPC in THF and converted to the actual Mn by dividing the GPC/THF Mn by 0.75 as concluded from the statistical analysis as described in

section 3.6. A set of molecular weights converted to the actual values is shown in Table 4.2.

Table 4.2 PDMA-29 converted Mn

Sample	GPC/THF [g/mol]	Polydispersity	GPC converted to actual value [g/mol]
B	2,100	1.21	2,800
C	2,500	1.18	3,300
D	3,300	1.22	4,400
E	4,900	1.20	6,400

The GPC/THF curves for all PDMA-29 samples are shown in Figure 4.4

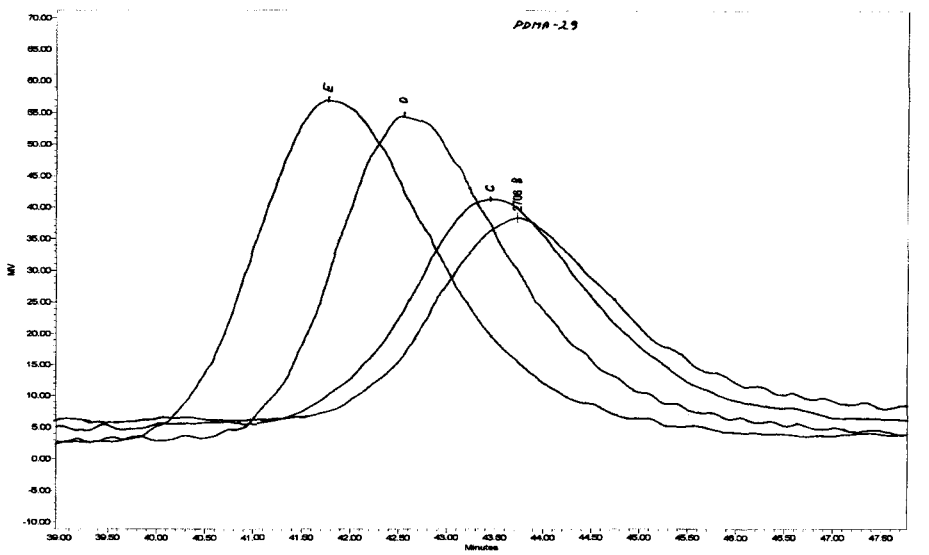


Figure 4.4 GPC in THF for PDMA-29-B,-C, -D, -E

All kinetic data are summarized in Table 4.3

Table 4.3 Kinetic data for PDMA-29

Sample	Time [s]	conversion x	-Ln(1-x)	degree of polym. Pd	[M]
	0	0	0	0	1
B	180	0.4	0.51083	28	0.6
C	360	0.48	0.65393	33	0.52
D	840	0.75	1.38629	44	0.25
E	1800	0.97	3.50656	64	0.03

The kinetic data obtained from the experiments allow the determination of the propagation rate constant k_p as indicated in the rate equation 4.2.[62,63,64,65,66]

Equation 4.2 Rate equation

$$\ln\frac{[M]_0}{[M]} = k_p \cdot [C^*] \cdot t$$

The semilogarithmic plot of –ln(1-x) versus experiment time shows a linear relationship between conversion and time.

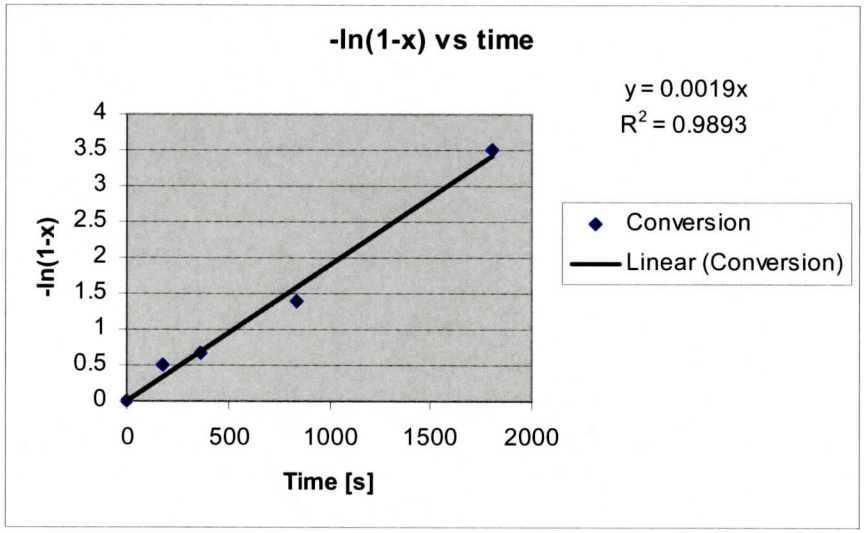


Figure 4.5 PDMA-29 conversion versus time.

The slope gives k_{obs}, which is equal to $1.9 \cdot 10^{-3}[\frac{1}{s}]$. The straight line indicates that, no chain transfer or crosslinking occurred during the polymerization.

The dependence of the degree of polymerization *Dp* on conversion x is shown in Figure 4.6.[66]

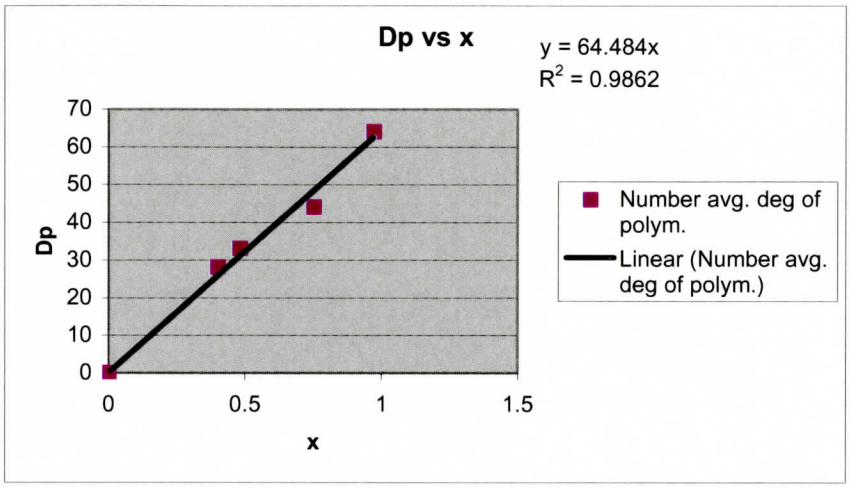


Figure 4.6 PDMA-29 *Dp* versus *x*.

The number average degree of polymerization *Dp* is linearly dependent on the conversion x according to Equation 4.1.

4.2 Discussion

The above kinetic data provides the basis for discussion related to the livingness of polymerization. The anionic polymerization of poly(dimethylacrylamide) will be analyzed accordingly to Hsieh's and Quirk's[67] criteria for living polymerization.

The first criterion refers to the monomer consumption. Polymerization continues until all monomer molecules are consumed and further addition of monomer resumes polymerization. Although no additional monomer was added to prove the evidence of further polymerization, all the monomer was incorporated to the macromonomer chains.

There was no monomer left in the reactor after termination. The molecular weight of the final product was in agreement with the calculated values.

The second criterion refers to the linearity of the number-average molecular weight, Mn function versus conversion x. The curve shown in Figure 4.6 proves this fact. The regression analysis with R^2 equal to 98.6% indicates a good fit of the curve to the sampling points. This is a rigorous criterion for living polymerization.

The number of polymer molecules (active centers) is constant and independent of conversion. This criterion is represented by Equation 4.1. The values obtained from PDMA-29 are in the range 0.017 to 0.020 mol/l. The concentration of living chain ends are relatively constant. The variation of 0.003 mol/l may contribute to the measurement error, since samples were taken from four different reaction vessels.

The fourth criterion is that the molecular weight can be controlled by the stoichiometry of the reaction. During the polymerization, termination of living chains can occur if impurities are present. The system is very sensitive to environment. Living chain ends can be destroyed by water or other impurities. As a result, the polymer molecular weight will be increased. If a chain transfer reaction takes place, the weight-average molecular weight of will be increased.

The fifth criterion refers to the polymer polydispersity. In a living polymerization the polydispersity should be low and follow Poisson distribution. Low polydispersity can be achieved when the initiation rate is much higher than that of propagation. All chains grow for the same period of time. The presence of aggregated initiator molecules can inhibit initiation and shift equilibrium between dormant and active centers towards dormant species. As a result, initiation slows down and gives high polydispersity. The addition of triethylborane coordinating agent helped in deagregation of initiator molecules and established the system for fast initiation that resulted in low polydispersity macromonomer.

The high polydispersity of an isotactic macromonomer was caused by the insufficient mixing in relation to the fast propagation. The polymer precipitated in a very short time after the monomer addition.

The next criterion involves the synthesis of block copolymers, as they can be produced by sequential monomer addition. This study did not include block copolymerization.

The seventh criterion deals with chain-end functional polymers that can be prepared in quantitative yields. This study proved that the macromonomer with a double bond end functional group can be synthesized by an anionic mechanism. The proper control of survived chain end functional group was difficult to achieve, possibly due to interaction of coordinating agent with active species.

The last criterion is supported by Figure 4.5, which represents the relationship between monomer concentration and time. In a living polymerization, the propagation rate should follow pseudo first order behaviour. If the concentration of active species is constant, Equation 4.2 holds, and the plot of $\ln([M]_0/[M])$ as a function of time should give a straight line, which is observed in Figure 4.5.

CHAPTER 5

Conclusions and recommendations

5.1 Conclusions

The purpose of this study was to synthesize poly(dimethylacrylamide) macromonomer by an anionic polymerization. The macromonomer should be soluble in the reaction solvent, THF. It was also planned to find the polymer evaluation methods that would show how well the process could be controlled.

The research strategy was to:

1. Establish the anionic polymerization system for macromonomer synthesis.
2. Find the proper formulation for the polymerization to achieve solubility of the macromonomer in the reaction solvent.
3. Find the method for determining the molecular weight of the macromonomer, to show the process control capabilities.
4. Determine the fraction of survived chain end functional group.
5. Investigate the influence of triethylborane coordinating agent on macromonomer tacticity and solubility in THF.
6. Perform the kinetic studies on the macromonomer synthesis.

The anionic polymerization system gives polymers with narrow polydispersity, but it requires a detailed preparation of the reactants and the reactor to remove impurities. The process is very sensitive and prone to the termination. The polymer molecular weight increases due to the termination of growing centers if water or other impurities are present. Although the actual polymerization is fast, extensive time is needed to prepare the system.

It was shown that the polymerization of dimethylacrylamide with diallylamine and *sec*-butyllithium produced polymer product insoluble in the reaction solvent. This research study included testing four coordinating agents, their different concentrations,

and two initiators for influencing the polymer solubility in THF. Only triethylborane yielded a polymer product that was soluble. The reaction performed at 0°C with triethylborane, diallylamine, and *sec*-butyllithium did not give any precipitate in THF. Triethylborane coordinated with the growing anion during propagation and sufficiently separated it from cation. This counterion separation enabled the system for syndiotactic and atactic monomer addition modes to the growing polymer chain. It produced solubility of the polymer in the reaction solvent.

The indication of polymerization control could be achieved by comparing the polymer molecular weight measured with the calculated value. The GPC was used to evaluate the macromonomer molecular weight.

The most accurate measurements were done with dimethylformamide as a mobile phase with 0.01 molar lithiumbromide. The polymer measurements performed in THF eluent gave a consistently low molecular weight, an average of 24 % lower than the calculated values. The macromonomer coils were shrunk in THF and did not give actual polymer sizes. The polydispersities measured in THF were low as predicted for the anionic system. The high polydispersity measured in dimethylformamide was attributed to the poor quality of GPC columns.

GPC measurements also showed that the studied polymerization was highly exothermic. The fast monomer addition, at a high reactor loading, gave high polydispersity and bimodal distributed polymers. The propagation was fast compared to the reactor mixing. The lack of molecular weight control in these experiments, which produced insoluble polymers, was caused also by fast propagation and inability of the system to achieve proper mixing.

The fraction of survived chain end functional group of the macromonomer was determined by ^{1}H NMR measurements. The ratio of the signal strength between protons associated with the double bond end functional group that originated from diallylamine to one of the monomer protons was possible to be determined due to the low polymer

molecular weight. This analysis showed that, the proper yield control was not satisfactory. There were some indications, that higher reactor loading or low concentration of coordinating agent decreased the macromonomer yield. Also, the strength of ligand can influenced the survived chain end double bond fraction.

The ^{13}C NMR measurements to quantify the stereoregularity of macromonomers showed that, in order to produce the solubility of polymer in THF, a 1.5 molar ratio of coordinating agent to initiator was required to give soluble polymer. There was only 23 % fraction of the isotactic structure.

If isotactic structure accounts for more that 30 %, then the polymer precipitates in THF.

As for the mechanism, the ligand coordinated with the growing polymer chain and isolated the cation, so that it did not influence the isotactic mode of the monomer addition.

The kinetic study showed that the reaction at –7 °C could be completed within 30 minutes after the monomer addition. It produced the polymer with 100 % yield. The process had a living character. There was no termination and no chain transfer. The degree of polymerization versus conversion and the conversion versus time had linear relationships. The propagation rate constant k_{obs} was equal to $1.9 \cdot 10^{-3}[\frac{1}{s}]$.

5.2 Recommendations

Based on the experimental results obtained in this research project, the following recommendations are made:

1. The low degree of macromonomer yield control indicates the need for further screening of coordinating agents and their concentrations. Triethylborane

might be too strongly coordinating with the growing polymer chains and destroying the functionality of the end group.

2. A more detailed kinetic investigation is recommended in order to fully understand the process mechanisms. The follow-up experiments should include the monomer and initiator variations to determine the reaction rates with respect to each of these reactants. Also the Arrhenius plots of the overall rate constants could be prepared based on kinetic experiments. These experiments could reveal information pertaining to the aggregation of the initiator or growing active chains and at the same time give a clear understanding of the interactions between the species competing for propagation. This would allow for the comprehension of the tacticity and solubility mechanisms.

3. The macromonomer should be used in further polymerization experiments to synthesize the copolymers.

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