INSTITUTO POLITÉCNICO DE BRAGANÇA
Escola Superior de Tecnologia e Gestão

Surfactant-free emulsion polymerization by "Grafting from" Polyvinylamine Stabilizer

Catarina Pereira Gomes

Final Dissertation submitted to

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Oriented by:

Professor Rolando Carlos Pereira Simões Dias

Professor Jose Ramon Leiza

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The experimental part of this work was carried out in Institute for Polymer Materials (POLYMAT) of the University of the Basque Country in San Sebastian, Spain.

Dedicated to my parents, my brothers, my sister in law and my nephews, for all love, dedication, without your strength I would never have achieved this goal in my life.

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Abstract

Emulsion polymerization technique is one of the most common techniques employed in industry to synthesize a wide range of polymers due to its versatility, the possibility to control the properties of the final product and because it is an environmentally friendly technique. Nevertheless, large amounts of surfactant are usually required to stabilize the system which can have deleterious effects on water resistance and on the mechanical properties of the polymer. Among the different techniques employed to circumvent this problem, recently, graft copolymerization of a monomer from water-soluble polymers containing amino groups has been employed to synthesize polymer particles with amphiphilic core-shell nanostructures. Applications of these particles include controlled release drugs, water-borne coatings and diagnostic testing.

In this project, water-soluble poly (N-vinylformamide) (PNVF) of different molecular weights was synthesized and characterized. Subsequently, the basic hydrolysis of these polymers was accomplished to obtain poly (vinyl amine) (PVAm) in an easy and controlled way. The synthesized poly (vinyl amines) were then employed as stabilizers in the surfactant-free emulsion polymerization of methyl methacrylate (MMA). The MMA monomer polymerizes via two different ways, grafting from polyvinylamine and homopolymerization, leading to a core-shell type particles with polyvinylamine-based shells. The effect of different variables such as initiator type and concentration, the pH of the reaction and the molecular weight of PVAm's on the conversion, grafting efficiency and morphology of the polymer particles were investigated. Throughout all the work, an extensive characterization of the polymers obtained in each step was performed in order to clarify possible mechanisms involved in this polymerization process. For the characterization of the polymeric particles obtained during this work were used some characterization techniques such as AF4, NMR, DLS, TEM, SEC/GPC and FT-IR.

Keywords: Surfactant free emulsion polymerization, poly (N-vinylformamide), poly (vinyl amine), poly (methylmetacrylate), graft copolymerization.

Resumo

A Técnica de polimerização em emulsão é uma das técnicas mais comuns utilizadas na indústria para sintetizar uma vasta gama de polímeros, devido à sua versatilidade, à possibilidade de controlar as propriedades do produto final e também porque é uma técnica "Amiga do Ambiente". No entanto, grandes quantidades de surfatante são geralmente necessárias para estabilizar o sistema, o que pode ter efeitos prejudiciais sobre a resistência à água e sobre as propriedades mecânicas do polímero. Entre as diferentes técnicas utilizadas para contornar este problema, recentemente, a "Graft copolymerization" de um monómero com polímeros solúveis em água contendo grupos amina foi utilizada para sintetizar partículas de polímeros com nanoestruturas anfifílicas do tipo núcleo-casca. Aplicações destas partículas incluem medicamentos de liberação controlada, revestimentos à base de água e testes de diagnóstico.

Neste projeto, foi sintetizado o polímero solúvel em água poli (N-vinilformamida) (PNVF) com diferentes pesos moleculares tendo também sido realizada a sua caracterização. Subsequentemente foi realizada a hidrólise básica desses polímeros, obtendo poli (vinilamina) (PVAm). A poli (vinilamina) sintetizada foi utilizada como estabilizador na polimerização em emulsão livre de surfatante do metilo metacrilato (MMA). O monómero MMA polimeriza através de dois processos diferentes a partir de enxertia de poli (vinilamina) e homopolimerização que conduz a um tipo de partículas com núcleo e camadas à base de poli (vinilamina).

Foi estudado o efeito de diferentes variáveis, tais como a concentração do iniciador, o pH da reação e o peso molecular de PVAm, tendo sido avaliado o seu efeito na conversão de monómero, eficiência de enxerto e na morfologia das partículas de polímero. Para a caracterização das partículas poliméricas obtidas ao longo deste trabalho foram utilizadas as seguintes técnicas: AF4, NMR, DLS, TEM, SEC/GPC and FT-IR.

Palavras-chave: Polimerização em emulsão livre de surfatante, Poli (N-vinilformamida), poli (vinilamina), poli (metilmetacrilato), "graft copolymerization".

Contents

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Nomenclature

AF4- Asymmetric- Flow Field Flow Fractionation

AIBA- 2.2-Azobis (2-methylpropionamide) dihydrochloride

CMC- Critical Micelle concentration

^{13}C NMR – Carbon Nuclear Magnetic Resonance Spectrometry

D_2O- Deuterated water

DSC- Differential Scanning calorimetry

FRP-Free radical polymerization

FT-IR-Fourier Transform Infra-Red Spectroscopy

GE- Grafting efficiency

^{1}H NMR – Proton Nuclear Magnetic Resonance Spectrometry

HSQC NMR- Heteronuclear Single Quantum Coherence Nuclear Magnetic Resonance Spectrometry

HCl- Hydrochloric acid

I- Initiator

KPS- Potassium Persulfate

k_i- Initiation rate constant

k_d- Dissociation rate constant

k_p- Propagation rate constant

k_{tc}- Termination by combination rate constant

k_{td}- Termination by disprotonation rate constant

$k_{tr,\ TA}$- Chain transfer rate constant

TA- Transfer Agent

T- Group that transfer

A•- Radical generated by transfer reaction

M- Monomer

Mw- Weight average molecular weight

Mn- Number average molecular weight

MMA- Methylmetacrylate

NaOH- Sodium hydroxide

N_2- Nitrogen

NMR- Nuclear Magnetic Resonance

NVF- N-vinylformamide

PNVF- Poly (N-vinylformamide)

PMMA- Poly (methylmetacrylate)

PVAm – Poly (vinylamine)

rpm- Rotations per minute

R•- Free Radical

RC1- Reaction Calorimeter

RMn•- Growing polymer chain, n= number of repeating units

SC – Solids contents

SEC/GPC- Size Exclusion Chromatography/Gel Permeation Chromatography

TBHP- Tert-butyl hydroperoxide

THF- Tetrahydrofurane

TEM- Transmission Electron micro

Chapter 1

1.1 Introduction

Water-soluble polymers find numerous applications, including cosmetics detergents, oral care, water purification, pulp and paper production, oil recovery, sugar refining, biomedicine, pharmaceutical applications, and biotechnology.[1]They have the potential of creating a wide variety of functional polymers. To control and enhance the performance of water-soluble polymers in these applications, the polymerization kinetics and mechanisms are required to be well understood. Water-soluble polymers are often synthesized via Free Radical Polymerization (FRP). The polymerization is accompanied by solvent effects, as water gives rise to interactions in the polymerization system.[2]

N- Vinylformamide (NVF) is a water soluble monomer, which is a precursor to the amide and amine functional polymers and other functional polymers.[3] The properties of NVF are the high reactivity and the ideal mild hydrolysis under acid or base conditions even after polymerization.[4] NVF is the key compound in the synthesis of linear cationic polymers with reactive primary amino groups.[5]

Free-radical polymerization is the most convenient method to produce poly NVF, although other methods have been studied including cationic[6,7] and anionic[8] polymerizations. Only in a few papers the kinetic polymerization of NVF in aqueous solution is described. Gu et al. investigates the free-radical polymerization of NVF in aqueous solution and in bulk.[9] Free-radical polymerization of NVF carried out by Schmidt et al.[10] in a differential scanning calorimeter was used to estimate $k_p/k_t^{1/2}$ values.

The industrial interest in PNVF can be traced back to poly (vinylamine) (PVAm). PVAm is an attractive polymer since it possesses the highest known charge density along the polymer backbone at appropriate pH and high reactivity of primary amine-pendant groups. As one of the simplest polycationic polymers, it is in principle an ideal model for the simplest representative of a group of weak poly-bases in polyelectrolyte studies. Because of its pH dependent nature, it is possible to easily control the ionic properties, such as the charge density and acid-base strength, by simple protonation.[11] Thus it has been employed in a variety of applications, for example, as chelating ligands for various heavy metal ions[12,13], carriers for the immobilization of enzymes[14,15], flocculants in

wastewater treatment[16-18], finishing agents in textile modification[19, 20], and the pretreatment for the salt-free dyeing of cotton with reactive dyes[21], etc.[11]

PVAm is also of interest because of its nucleophilic nature. The high activity of the amino groups provides the polymer significant modification possibilities, which make it suitable to be used as starting material for the preparation of a variety of important functional materials.[22-24]For instance, PVAm has been modified with various reactions to prepare nitrogenous resins[22], water-soluble polymeric dyes [25-29], thermo-sensitive and/or pH-sensitive polymers,[30-32] photo-sensitive polymers,[33,34]chromophoric water-soluble polymers,[35, 36] polymers catalysts[37-39], polymer surfactants,[40] and so on. Hence, PVAm is not only of theoretical importance, but also of practical significance. However, PVAm cannot be obtained through the direct polymerization of N-vinylamine because the monomer is not available due to its tautomerization to acetaldehyde imine.[41] Thus PVAm can only be synthesized indirectly via Hofmann degradation of polyacrylamide[42-44] or hydrolysis of preformed polymers such as poly (N-vinylformamide).[11, 45, 46]

The goal of the present work was following: First the synthesis of poly (N-vinylformamide) with different molecular weights and different degrees of hydrolysis. The second objective was to carry out synthesis of surfactant-free emulsion polymerization of methyl methcrylate (MMA) using previously synthesized poly (vinylamine) as stabilizer. The effect of the ratio between the polyvinylamine and the initiator (TBHP and KPS) as well as the molecular weight of the poly (vinylamine) on the stability of the final latexes and the particle diameter was studied. Along the work, a deeply characterization of the synthesized products was performed for understand the process.

1.2. Organization of the Dissertation

Chapter 1 intends to introduce the topic of this thesis in the current framework and present the primary aim of the project. In Chapter 2 some general concepts about the theme, and the different methods for the synthesis used in experimental part of this project are described.

Chapter 3 is intended for the exposure of the main equipment, reagents and the procedures to be used in the course of scientific research.

Chapter 4 presents the results obtained in some experiments, using different analyses and Chapter 5 contains a brief conclusion about all work.

The bibliographic references are presented at the end of each chapter.

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Chapter 2

Bibliographic Revision

2.1 Water soluble polymers

Water-soluble polymers, which possess various useful properties such as thickening, gelling, flocculating, rheology modifying and stabilizing in any given application, are used for a wide variety of applications including food processing, water treatment, paper, enhanced oil and natural gas recovery, mineral processing, detergents, textiles, personal care products, pharmaceuticals, petroleum production, and surface coatings. These polymers can be categorized into following three groups: Synthetic, which are produced by polymerization of monomers synthesized from petroleum or natural gas; derived raw materials: semisynthetic, which are manufactured by chemical derivatization of natural organic materials, generally polysaccharides such as cellulose: natural, including microbial, plant and animal derived materials.[1] In terms of volume, about 60 % of the water-soluble polymers used in 2012 were from synthetic origin, 25% natural and 15% semisynthetic.[1]The following pie chart shows world consumption of water-soluble polymers:

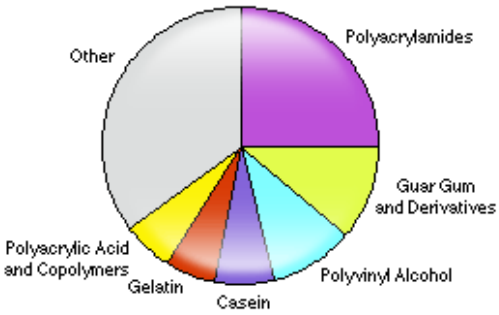


Figure 1. World consumption of water- soluble polymers-2013.[1]

Generally, water-soluble polymers are divided into two groups: non-ionic and ionic polymers. Their water polymer solubility is achieved by ionic and non-ionic polar functional groups. Those water-soluble polymers that possess a certain type of charge because of the interaction between polar functional groups and aqueous media are usually called polyelectrolytes. Polyelectrolytes fall into two sub categories, anionic and cationic polymers, depending on their charge types.[2]

Water-soluble polymers can be obtained from natural sources, such as starch and cellulose, or be synthesized, such as polyacrylamide (PAM) and polyethylene oxide (PEO). Synthetic water-soluble polymers offer the following advantages: product consistency, reliable supply, chemical and biological stability, and the ability to be tailored to a specific application by varying monomers and synthetic methods.[2]

This chapter provides background information on poly (N-vinylformamide) (PNVF), this polymer is a non-ionic type polyelectrolyte. After hydrolysis, it becomes polyvinylamine (PVAm), which is cationic at low pH values, pH<3.

This chapter also provides background information on the different types of polymerization used to produce PNVF and PVAm, as well the understanding of the mechanisms and kinetics involving the polymerization.

2.1.1. N-vinylformamide

N-vinylformamide is the simplest member of N-vinylamide family. It is developed as a precursor to amide and amine functional polymers. The first synthesis was made in 1965 by Kurtz and Disselnkoetter. A recently developed production technology used two simple chemicals, acetaldehyde and formamide, to synthesize the precursor of NVF, ethylidene formamide. The formamide was then heated to produce NVF using a catalyst. Figure 2 shows one of the synthetic routes (Stinson, 1993) of NVF, PNVF and PVAm, including the steps of polymerization and hydrolysis.

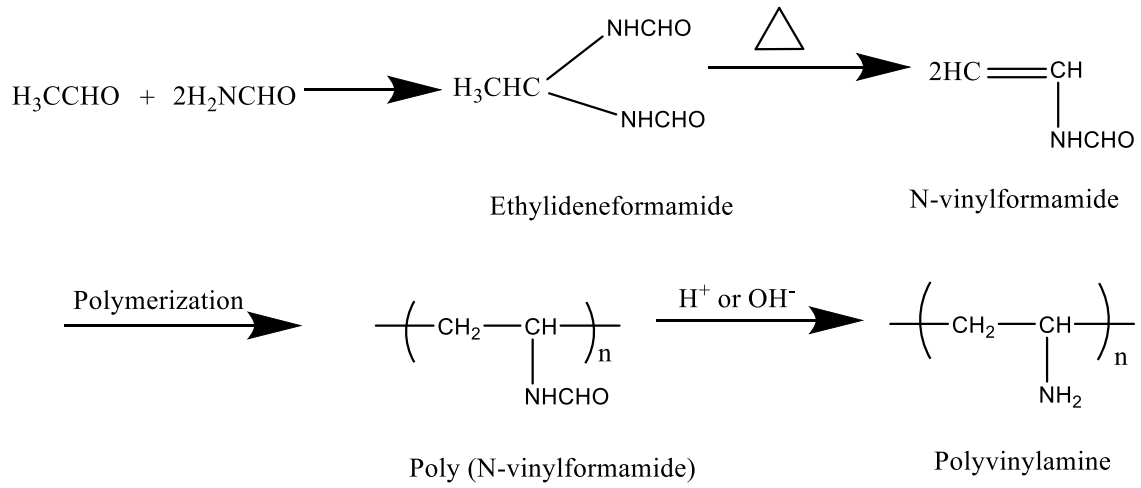


Figure 2. Synthesis of NVF, PNVF and PVAm (Stinson, 1993)

This has become the only commercially attractive route now. Air Products and Chemicals (The development has now been discontinued) (1986), BASF (1983) and Mitsubishi Chemical Corp (1996), all developed similar technologies to produce NVF through cracking of ethylidene formamide.[2]

NVF is a water soluble, colorless liquid, which dissolves in most polar solvents, such as methanol, ethanol, chloroform and THF.[2] It has a molecular weight of 71 g/mol and a high boiling point of 80 ºC at 10 mmHg. NVF is a water soluble monomer that provides a wider range of application due to its lower toxicity and higher reactivity than the most common acrylamide monomer. NVF has showed attractive high reactivities in polymerization, copolymerization and hydrolysis. NVF is stable and can be stored at room temperature for months. The commercial product usually has a light yellow color due to the added inhibitor.[3]

2.2. Methods and synthesis

2.2.1. Free- Radical Polymerization

In free radical polymerization, the formation of NVF polymer chains consists of four kinetic stages, initiation of the active monomer, propagation, termination of the active chain to give the final polymer product and the chain transfer. The main side reactions are chain transfer to monomer and polymer.[4]

Other mechanisms that can affect this process include the inhibition or retardation of free radical initiation, chain transfer of the radical centre to other molecules in the reaction medium, and branching reactions.[5]

2.2.1.1. Mechanisms of FRP

- ✓ **Initiation**

During the initiation, an active centre is created from which a polymer chain is generated. Initiation has two steps. In the first step one or two radicals are created from the initiating molecules. In the second step, radicals are transferred from initiator molecules to the monomers units present.

During this project, three types of initiators were used: in solution polymerization AIBA (2, 2'-Azobis (2-methylpropionamide) dihydrochloride, purity 97%, Sigma-Aldrich) was used and for the emulsion polymerization reactions TBHP (Luperox

TBH70X, tert-butyl hydroperoxide 70 wt% in H_2O, Sigma- Aldrich) and KPS (Potassium Persulfate, purity 99%, Sigma- Aldrich) were used Table 1 shows the molecular formula and structure of the compounds used in the experimental part of this work and Table 2 presents a compilation about their properties

Table 1. Molecular formula and structural of the initiators used in the experimental part of this work. (Sigma-Aldrich)

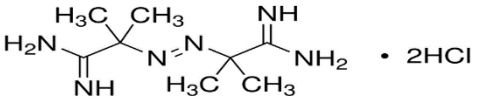
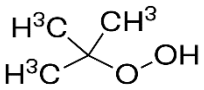
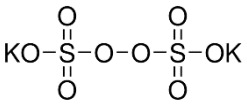
Initiator	Molecular Formula	Molecular structure
AIBA	$C_8H_{20}N_6Cl_2$	
TBHP	$C_4H_{10}O_2$	
KPS	$K_2S_2O_8$	

Table 2. Properties of the initiators used in the experimental part of this project. (Sigma-Aldrich)

Initiator	Properties	Conditions	Value	Units
AIBA	Molecular weight	-	271.19	$gmol^{-1}$
	Form		Granular	
	Solubility		Water, methanol, acetone, dioxane, ethanol	
	Insolubility		Toluene	
	Activity energy	-	124	$KJmol^{-1}$
	Melting point	-	170-175	ºC
	Decomposition Temperature	-	56 -	ºC -
	Boiling point	760 mmHg	267	ºC
	Half-time		10	h

Initiator	Properties	Conditions	Value	Units
TBHP	Molecular weight	-	90.12	$gmol^{-1}$
	Density	-	0.93	g/mL
	Melting point	-	-3	ºC
	Boiling point		96	ºC
	Solubility	Water		
	Refractive Index		1.386	-
KPS	Molecular weight	$gmol^{-1}$	-	270.32
	Density	gcm^{-3}	-	2.477
	Solubility		Water	
	Insolubility		Alcohol	
	Melting Point	ºC	-	<100
	Refractive index	-	-	1.467

✓ **Propagation**

Rapid growth of the chain occurs by monomer reacting with the active center on the chain, generating a new active center. The concentration of active centers in the polymerization medium is usually kept low (less than 0.1 wt. % initiator).[5] This results in low numbers of polymerizing chains and a high probability that the radical center will react with monomer rather than other molecules. On the average, the chains can grow to long macromolecules before terminating.[6]

✓ **Termination**

The termination mechanism is a function of the monomer, the temperature and the viscosity of the medium. Chain termination can occurs by several different mechanisms.[7,8]

- Combination of two active chain ends, by combination or radical disproportionation. Both reactions yields to lead polymers chains that no longer propagate. Combination occurs when the two chain ends approach along their lines of centers and a carbon-carbon bond is reformed between them.[5]
- Combination of an active chain end with an initiator radical.[5]

- Interactions with impurities or inhibitors; a common inhibitor is for example the presence of oxygen inside the reaction because if the growing chain will react with molecular oxygen producing an oxygen radical, which is much less reactive. This significantly slows down the rate of propagation.[5]

✓ **Chain Transfer**

Contrary to the other modes of termination, chain transfer results in the destruction of only one radical, but also the creation of another radical. Similar to disproportionation, all chain transfer mechanisms also involve the abstraction of a hydrogen atom. There are several types of chain transfer mechanisms:

- Chain transfer to Solvent: a hydrogen atom is abstracted from a solvent molecule, resulting in the formation of radical on the solvent molecules.
- Chain transfer to monomer: a hydrogen atom is abstracted from a monomer.
- Chain transfer to initiator: a polymer chain reacts with initiator, which terminates that polymer chain, but creates a new radical initiator. This initiator can then begin new polymer chains.
- Chain transfer to polymer: the radical of a polymer chain abstracts a hydrogen atom from somewhere on another polymer chain. This terminates one of the polymer chains, but allows the other to branch.[5]

The simplified equations for the different mechanisms in a classical free radical polymerization are present in Table 3.

Table 3. Main mechanisms that occurs in Free Radical Polymerization.[9]

	Mechanism	**Equation**
Initiation	Decomposition initiator	$I \xrightarrow{k_d} 2R^{\bullet}$
	Initiation monomer	$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet}$
Propagation		$RM_n^{\bullet} + M \xrightarrow{k_p} RM_{n+1}^{\bullet}$
Termination	Combination	$RM_n^{\bullet} + RM_p^{\bullet} \xrightarrow{k_{tc}} RM_n - M_pR$
	Disproportionation	$RM_n^{\bullet} + RM_p^{\bullet} \xrightarrow{k_{td}} RM_n + RM_p$
Chain Transfer		$RM_n^{\bullet} + T - A \xrightarrow{k_{tr,TA}} RM_n^{\bullet} + A^{\bullet}$

2.2.1.2. Aqueous solution polymerization

N-vinylformamide (NVF), a blocked vinylamine monomer, has become an important reagent in the synthesis of water-soluble resins. NVF can be easily polymerized in aqueous solution or in bulk.[10]

As a general trend, the solution polymerization is accompanied by solvent effects, as water might interact in the polymerization system.[11] Polymerization of a monomer in a solvent overcomes many of the disadvantages of the bulk process. It acts as diluent and aids in the transfer of the heat of polymerization. The solvent also allows easier stirring, since the viscosity of the reaction mixture is decreased. Thermal control is much easier in solution polymerization compared to bulk polymerization. On the other hand, the presence of the solvent may present new difficulties. Unless the solvent is chosen with appropriate consideration, chain transfer to solvent can become a problem. Further, the purity of the polymer may be affected if there are difficulties in removal of solvent.[9] In this work, poly (N-vinylformamide) was synthesized via free-radical polymerization in aqueous solution. The use of water as solvent makes the process environmentally friendly.

2.2.2. Hydrolysis of PNVF

Synthesis of polyvinylamine, PVAm, has been challenge for generations. The simplest monomer to provide this polyelectrolyte is not available because vynilamine, VAm, does not exist in a free state[12]. The common synthesis routes of PVAm involve modifications of the other polymers that are readily available, such as polyacrylamide (PAM)[13], polyacrylic acid (PAA)[14], polyacrylonitrile (PAN)[15], and poly (N-vinyl tert-butylcarbamate)[16,17]. These modifications, always complicated and costly, usually consist of a series of reactions followed by a final hydrolysis step to PVAm[18].

N-vinylformamide (NVF) was developed as a precursor for simple and economical production of PVAm. PNVF can be easily converted into PVAm by hydrolysis in either acidic or basic aqueous solution. Acidic hydrolysis produces cationic polymers, whereas base hydrolysis yields polymers with free amine functional groups. According to *Yamamoto et al*.[19] hydrolyses accomplished with base or acid media, if appropriate conditions exist, lead to 100% transformation of PNVF into PVAm. This suggests that the PVAm backbones consist exclusively of $-CH_2-CH(NH_2)-$ or $-CH_2-CH(NH_3^+)-$ units, respectively.[12]

In contrast, *Pinschmidt et al*.[20] maintained that such a complete transformation is only possible in the case of basic hydrolysis. If acid is employed, the conversion cannot surpass the 80% level due to mutual repelling of positive charges.[12] During the basic hydrolysis of PNVF, the byproduct sodium formate salt formed needs to be removed by dialysis or precipitation at a great expense for ulterior uses. In contrast, acid hydrolysis conducted in the mixture of methanol and aqueous solvent produces methylformate, which can be easily stripped as a light component.[18]An alternative approach recently developed was a catalyzed thermal hydrolysis.[21]The synthesis routes of PVAm via base or acid hydrolysis of PNVF are shown in Figure 3.

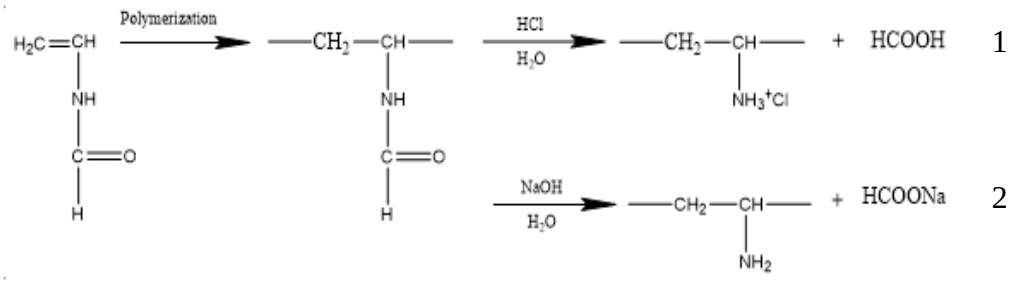


Figure 3. Scheme for synthesis route of polyvinylamine (PVAm) via 1) acid and 2) basic hydrolysis of poly (N-vinylformamide) (PNVF).[18]

Industrial interests in PNVF and its hydrolysis products are growing constantly because of its potential applications in various fields. This synthesis route will probably become the most effective approach to prepare high molecular weight polyelectrolytes and/or amine functional polymers.[18]

2.2.3. Emulsion Polymerization

Emulsion polymerization is a widely used process for the production of polymers used for adhesives, paints, binders, additives.[22] It is one of the most common ways of polymerization due to low viscosity of the product, easy heat removal as water is usually the continuous medium, good temperature control and high polymerizations rates.

The fundamental mechanism of emulsion polymerization is illustrated in Figure 4. This type of polymerization involves emulsification of the relatively hydrophobic monomer in water by an oil-in-water emulsifier, followed by the initiation reaction with either a water-insoluble or an oil-soluble free radical initiator[23]. The fundamental mechanism of emulsion polymerization usually starts with an emulsion incorporating water, monomer and surfactant. In a conventional emulsion polymerization the

continuous phase is composed of water in which droplets of monomer are emulsified. The polymerization occurs in the particles that form spontaneously in the first few minutes of the process. Typical monomers used in emulsion polymerization include butadiene, styrene, acrylonitrile, acrylate ester and methacrylate ester monomers, vinyl acetate, and vinyl chloride.[24]

At the end of the polymerization, a milky fluid called "latex", "synthetic latex" or "polymer dispersion" is obtained. Latex is defined as "colloidal dispersion of polymer particles in an aqueous medium". The polymer may be organic or inorganic. In general, latexes contain 40-60% polymer solids and comprise a large population of polymer particles dispersed in the continuous aqueous phase (about 10^{15} particles/mL of latex). Particles are within the size range 10 nm to 1000 nm in diameter and are generally spherical. A typical particle is composed of 1-10000 macromolecules, and each macromolecule contains about 100-10^6 monomers units.[25, 26]

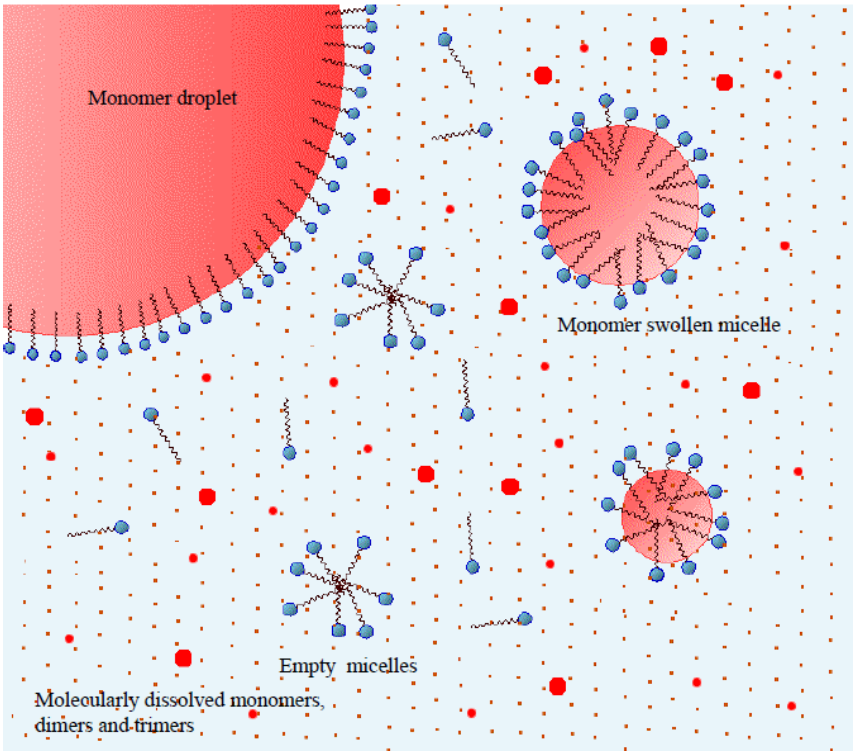


Figure 4. General mechanism of emulsion polymerization process.[27]

Harkins[28, 29], presented the first qualitative description of the mechanisms involved in emulsion polymerization. Based on Harkin´s description, Smith and Ewart[30] proposed the first quantitative model for batch emulsion polymerization where three intervals are distinguished.

In interval I, particle formation takes place and monomer droplets, surfactant (and micelles if above the critical micelle concentration, CMC) and precursor particles (a small, colloidal unstable particle that upon further propagation growth, coagulation and adsorption of surfactant will eventually grow to a colloidal stable 'mature' particle) are present. Interval II occurs after the conclusion of the particle formation period whereby only mature latex particles now exist; the particle number density (N_p, the number of particles per unit volume of the continuous phase) remains constant and the particles grow by propagation in the presence of monomer droplets. As the diffusion of monomer from a droplet to a particle is rapid on the timescale of polymerization, the droplets act as monomer reservoirs that ensure that the monomer concentration into the particles is essentially constant. Plotting monomer concentration as a function of particle size shows that the saturation concentration is, to a good approximation, constant for all except very small particles. Upon the exhaustion of these monomer droplets, Interval III commences, where the remaining monomer contained within the particles is polymerized.[24]

2.2.3.1. Surfactant-free emulsion polymerization

Emulsion polymerization is an important industrial process for the manufacture of polymeric materials with excellent water resistance and adhesion properties.[24]

In the past decade, the group of Li has been focusing on the development of simple and versatile routes to produce well-defined cationic amphiphilic core-shell particles based in redox initiation between alkyl hydroperoxide and the amine group of water-soluble polymer in water.[31, 32]

This approach is based on the reaction between alkyl hydroperoxide and the amino group of the water soluble polymer in water. Amphiphilic graft copolymers and hydrophobic homopolymers are generated concurrently, forming highly monodisperse particles with an amphiphilic core-shell structure. Figure 5 illustrates the formation mechanism of amphiphilic core-shell structure and Figure 6 shows the chemistry of the grafting copolymerizaion and homopolymerization. The hydroperoxide (ROOH) initially interacts with amino groups on the polymer backbone forming redox pairs. Electron transfer and loss of protons results in the formation of amino radicals and alkoxyl radicals (RO$^{\bullet}$). The amino radicals are capable of initiating the graft copolymerization of the vinyl monomers. The RO$^{\bullet}$ generated can either initiate homopolymerization of vinyl monomer or abstract a hydrogen atom from the polymer backbone, thus generating a backbone

radical that can also initiate the graft copolymerization of vinyl monomers. The amphiphilic graft copolymers generated in situ act like polymeric surfactants, self-assembling to form micelle-like microdomains. These polymeric micelles are able to assist the emulsion polymerization of the vinyl monomer. Therefore, the hydrophobic

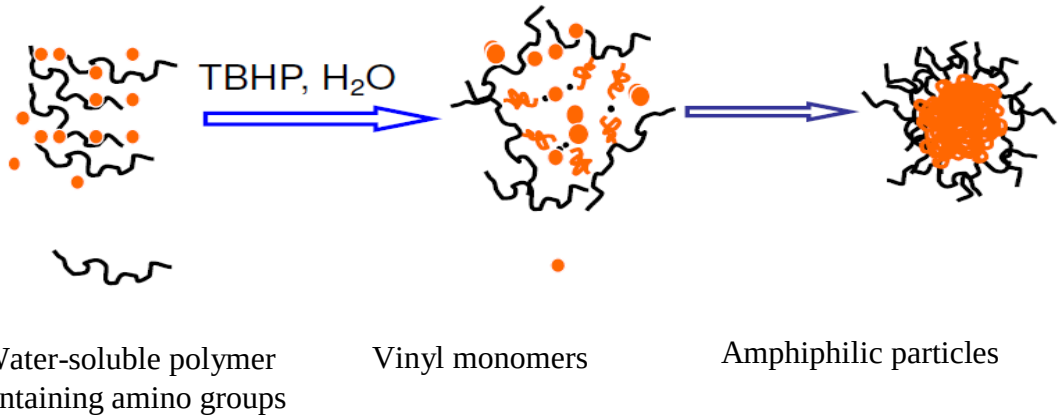


Figure 5.Schematic representation of the formation of amphiphilic core-shell nanospheres.[32]

vinyl monomer can undergo polymerization within the hydrophobic domains of the micelles to form core-shell particles with the water-soluble polymer as the shells.[33]

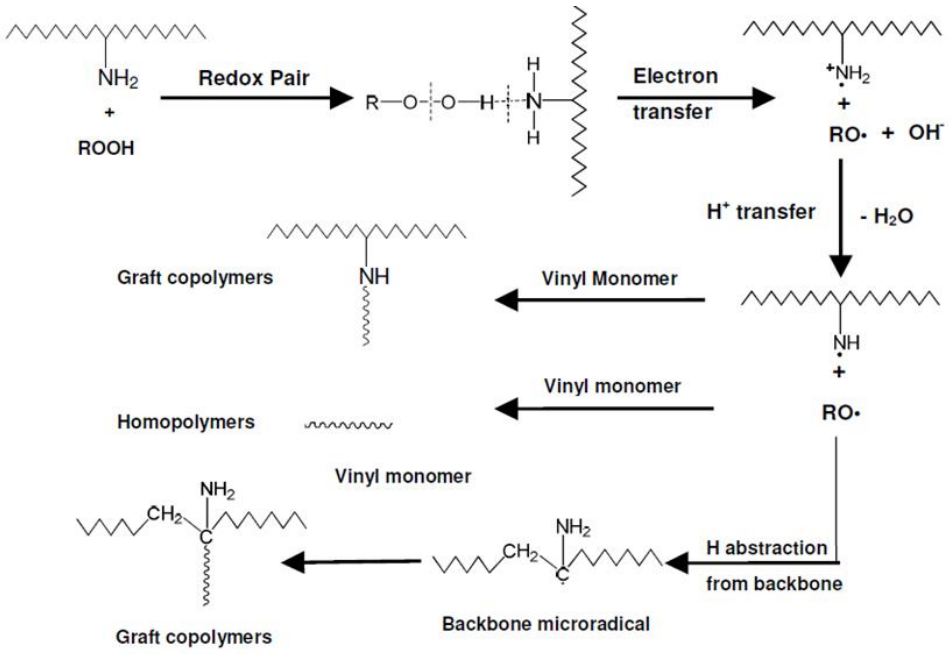


Figure 6 ıble polymer.

This is a versatile approach to prepare a wide range of core-shell particles with shells form natural biopolymers such as casein, gelatin, albumin, bovine serum and chitosan to synthetic polymers such as polyethyleimine (PEI), polyallylamine (PAAm), polyvinylamine (PVAm). Thus various amine rich core-shell particles can be easily prepared. These types of particles containing highly reactive amine groups are very useful materials because they can electrostatically bind to or covalently link with small (e.g. drug or dye molecules) or large molecules (negatively charged DNA, enzyme). Therefore, they have a great potential in diverse applications including enzyme immobilization or drug and gene deliveries.[34-37] In addition, the composition, functionality, rigidity, reactivity, shell thickness, core diameter, particle size and stability of the particles could be easily tailored through variations of the composition and structure of the shell polymers and the hydrophobic monomers.[33]

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Chapter 3

Experimental Section

The experimental part of this work was divided in three steps, first the kinetics and the mechanism involved in the polymerization of NVF in aqueous media were analyzed. For this purpose, the effect of temperature, concentration of initiator and concentration of NVF in the kinetics of the polyNVF produced was experimentally assessed. Under these conditions the second step was to synthesize poly (vinylamine) of different molecular weights and different degrees of hydrolysis. In this section the detailed characterization of the monomer and polymer was performed and the also hydrolysis conversion was calculated. Then, the synthesis of PVAm: PMMA particles by surfactant-free emulsion polymerization was performed using the previously synthesized poly (vinylamine)s. In the last step the conversion of the polymer, particle size diameter, particle size distribution, pH of final product, morphology of the PVAm: PMMA particles and the composition of PVAm: PMMA particles were studied.

3.1. Aqueous solution polymerization of NVF

3.1.1. Materials

N-vinyl formamide, NVF, (Aldrich, Madrid, Spain, 98%, stabilized with 25 to 50 ppm 4-hydroxy-Tempo) was distilled under vacuum and stored at -10 ºC. The free radical initiator 2, 2'-azobis (2-methylpropionamide) dihydrochloride (AIBA) (97%, Aldrich) was used as received. Distilled water was used for the preparation of the polymerization solutions.

With the objective to obtain a different molecular weight of polyNVF, polymerizations were carried out both in a jacketed reactor and in a Reaction Calorimeter (RC1) reactor under pressure. The jacketed reactor has a capacity of 1L and was equipped with a mechanical stirrer (turbine impeller), a pipe to withdraw samples, a pipe for nitrogen purging, a thermocouple and a reflux condenser. The RC1 has a capacity of 1L and was equipped with a magnetic drive stirred (turbine with pitched blades impeller), a Pt 100 sensor probe, a pump to control the pressure and a pipe for nitrogen purging. Figure7 presents the experimental setups used to carry out these synthesis.

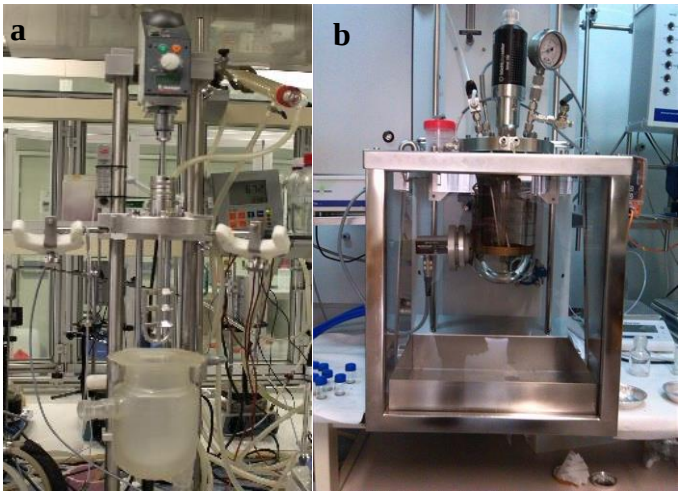

Figure 7. Experimental setups used for the synthesis of polyNVF a) jacketed reactor, b) RC1 reactor (pressurized reactor).

3.1.2. Procedure for the synthesis of polyNVF

In a typical reaction to synthesize polyNVF, an aqueous solution of the monomer was heated to the reaction temperature under constant stirring and nitrogen atmosphere. Once the reaction temperature reached the set-point value, polymerization was initiated by the addition of a known amount of a solution of AIBA initiator in distilled water. The different formulations used in these synthesis, in order to obtain different molecular weights of polyNVF, are presented in Table 4.

Table 4. Formulations employed in the synthesis of the polyNVF.

Name of the polyNVF	**Type of reactor**	**Time of reaction (min)**	**Temperature (ºC)**	**Concentration of NVF (wt %)**	**Concentration of initiator (mM)**
PNVF1	Jacketed	120	70	9	8
PNVF2	Jacketed	90	85	6	3,2
PNVF3	Jacketed	60	90	4	8
PNVF4	RC1	60	100	4	4

3.1.3. NVF and PolyNVF Characterization

The composition of the monomer (NVF) was analyzed by nuclear magnetic resonance spectroscopy, ^{1}H NMR, HSQC and ^{13}CNMR. These results were recorded in a Bruker spectrometer DRX-500. Chemical shifts are reported in ppm downfield and the solvent peak of deuterium oxide (D_2O) was used as reference. The sample solutions contained 0.4 mg of PolyNVF were dissolved in 0.07 mg D_2O. The working frequency was 400 MHz for ^{1}H NMR and ^{13}C NMR and 500 MHz for HSQC.

3.1.3.1. NVF Characterization

Figure 8 shows the generic structure of NVF, Figures 9 and 10 illustrate the ^{1}H NMR, and ^{13}C NMR spectra of them.

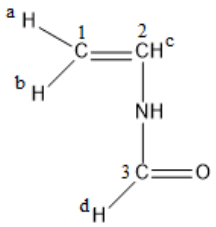

Figure 8. Chemical Structure of the monomer (NVF).

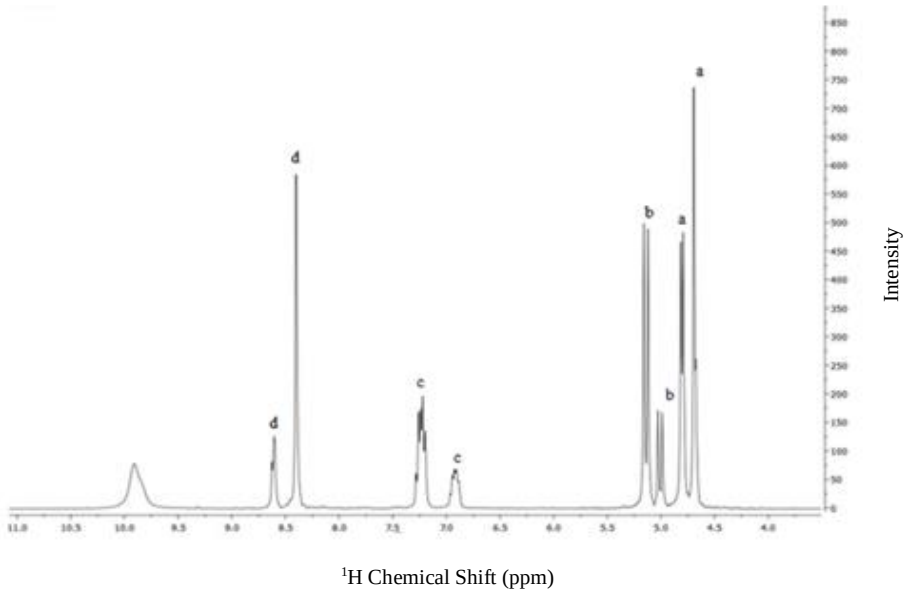

Figure 9. Illustration of ^{1}H NMR spectrum (400 MHz, D_2O) of the monomer (NVF) and respective assignment of the signals (Figure 8).

NMR or nuclear magnetic resonance spectroscopy is a technique used to determine a compound's unique structure. In Figure 9, it is possible to see that the chemical shift of the amide groups is at 8.0-9.0 ppm. The chemical shifts of the backbone –C**H**– and –C**H**$_2$ groups are at 6.75-7.5 and 4.5-5.5 ppm respectively, which are overlapped with the peak of H_2O in D_2O. The reason why all peaks showed two signals is due to the fact that these groups present a cis trans configuration.

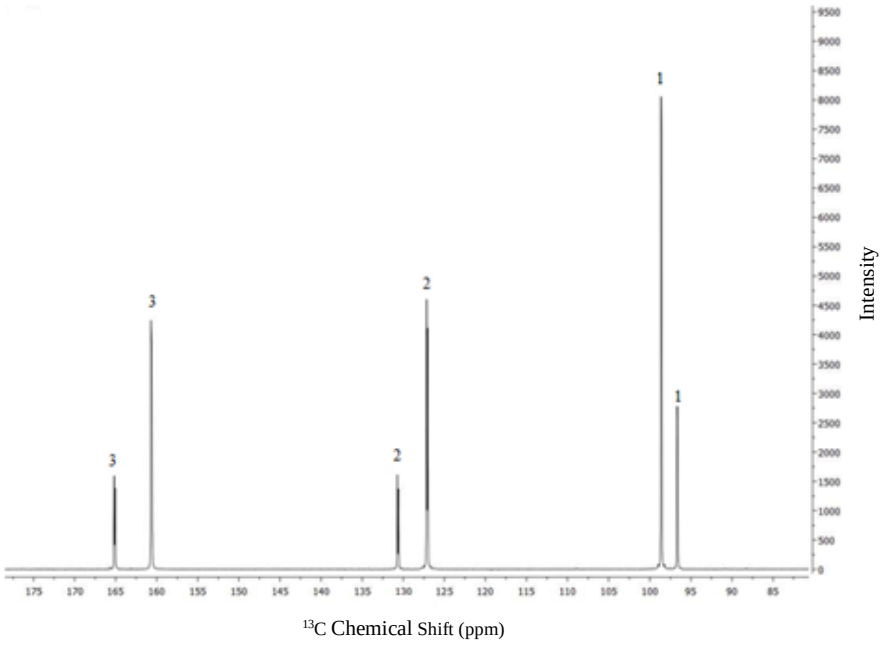

Figure 10. Illustration of ^{13}C NMR spectrum (400 MHz, D_2O) of the monomer (NVF) and respective assignment of the signals (Figure 8).

Because of the insufficient sensitivity of both ^{1}H and ^{13}C NMR analyses, the Heteronuclear Single Quantum Coherence (HSQC) NMR mode was applied.[1] HSQC is more sensitive than ^{13}C NMR because it is a proton- detected method that identifies cross peaks of proton with carbon signals, even if the latter peaks have relatively low intensity in high resolution ^{13}C NMR. This method is based on the 2D experiment that identifies correlation between ^{1}H with ^{13}C nuclei separated by more than one bond, and is highly suitable to recognize the carbon nuclei that do not have direct bond with hydrogen protons.[1] Figure 11 shows the HSQC NMR spectra of the monomer NVF. The 2D NMR spectra confirmed the analyses of both ^{1}H NMR and ^{13}C NMR presented above as it clearly demonstrated that C_1 interacted with H_a and H_b, C_2 with H_c and C_3 with H_d.

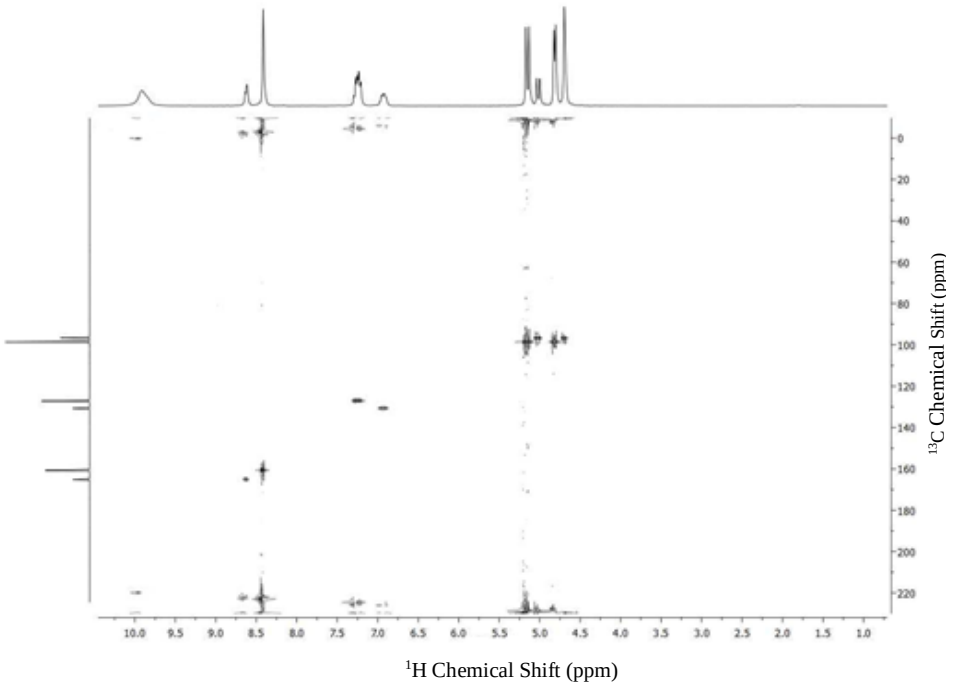

Figure 11. Illustration of HSQC NMR spectrum (500 MHz, D_2O) of the monomer (NVF).

3.1.3.2. Poly (NVF) characterization

The polyNVF composition was analyzed by ^{1}H NMR, ^{13}C NMR. Figure 12 present the chemical structure of poly (N-vinylformamide), Figure 13 show the ^{1}H NMR spectrum and Figure 14 show the ^{13}C NMR spectrum of polyNVF (PNVF3).

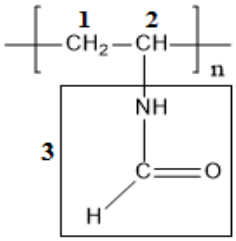

Figure 12. Chemical Structure of poly (NVF).

In the ^{1}H NMR spectrum of PNVF, the peaks about 1.4-1.9, 3.2-4.2 ppm, which are assigned to the protons referents to –C**H**$_2$– and –C**H**– groups of PNVF, respectively, were observed.[2] The peaks at 7.0-8.0 ppm are assigned to the proton of amide –NHC**H**O group. The peaks at 4.2-5.5 ppm, are attributed to the residual monomer (NVF), (see Figure 9 in chapter 3). Finally the peaks at 1.0-1.4 are referents to the residual part of the

initiator (AIBA), more information about ^{1}H and ^{13}C NMR of AIBA, is presented in Appendix I, section I.1.

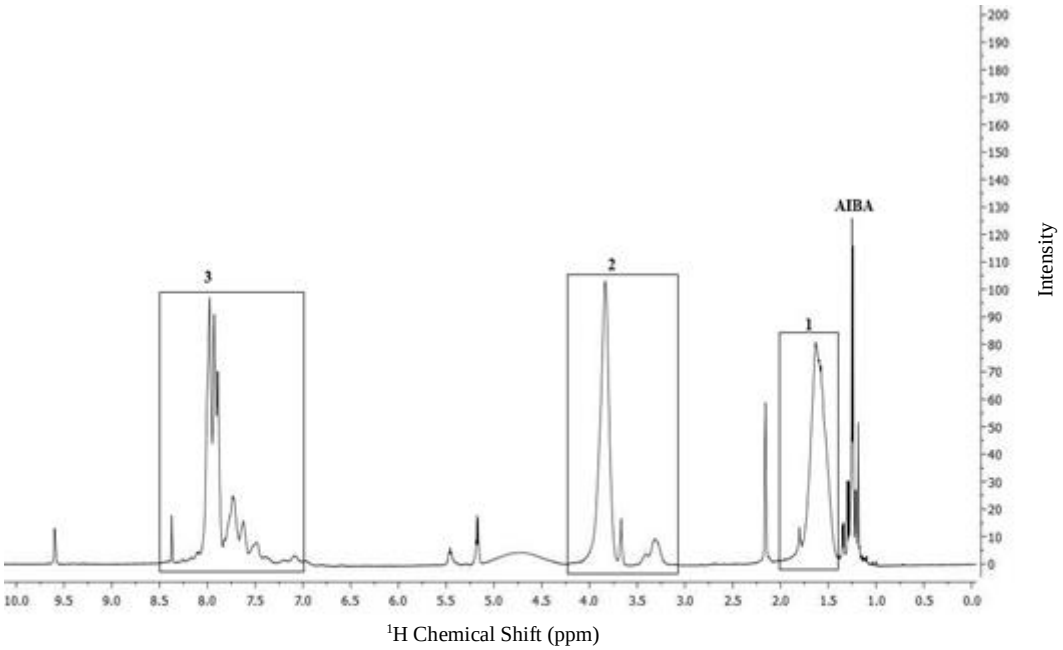

Figure 13. Illustration of ^{1}H NMR spectrum (400 MHz, D_2O) of the polymer PNVF3 and the assignment of the signals of the polymer structure (Figure 15).

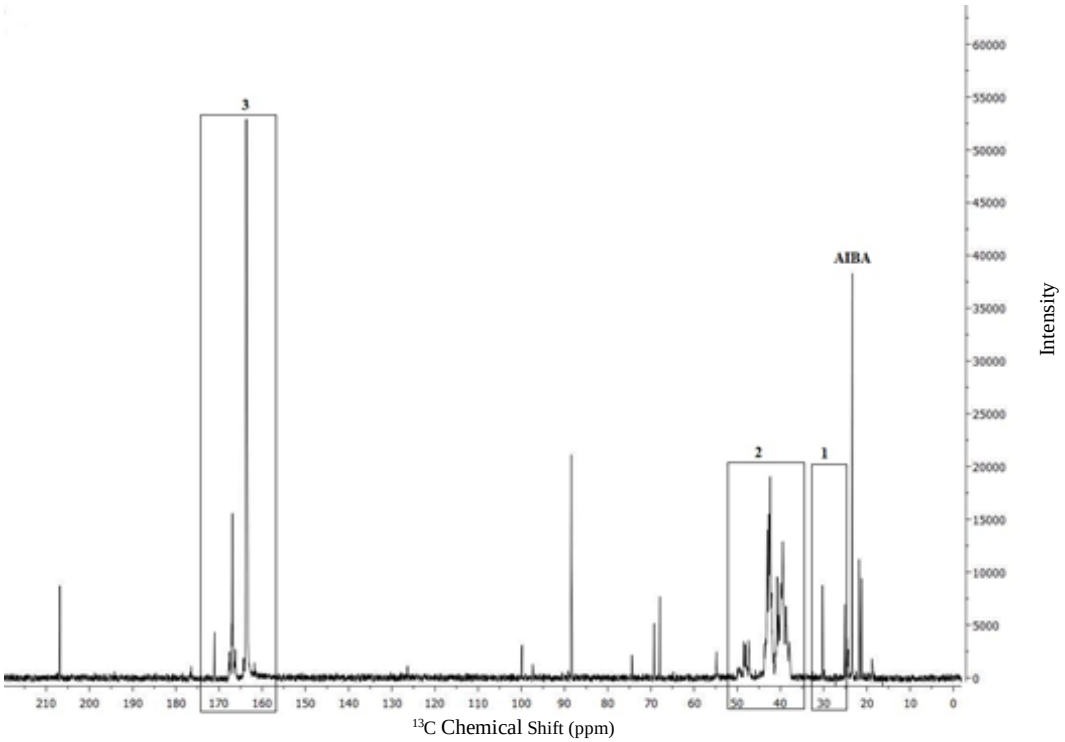

Figure 14. Illustration of ^{13}C NMR spectrum (400 MHz, D_2O) of the polymer PNVF3 and the assignment of the signals of the polymer structure (Figure 15).

In the ^{13}C NMR spectrum of PNVF, the peaks about 25-30 and 35-50 ppm, are assigned to the carbons on –**C**H2– and –**C**H– groups of PNVF, respectively. The peaks at 160-170 ppm are assigned to the carbon on –NH**C**HO group [3]. The other peaks which appear were analyzed and are referents to the residual monomer (NVF) and initiator (AIBA). The ^{13}C NMR spectrum of NVF is represented in Figure 10.

During the reaction samples were taken at different times and to stop further polymerization hydroquinone was added (1%). These samples were put in a vaccum oven at 50 ºC, during 24 hours. The polymerization conversion was calculated gravimetrically using the following equation:

$$\text{conversion (x)} = \frac{w_p}{M_0} \quad (1)$$

Where w_p is the mass of polymer and M_0 the initial mass of monomer.

The molar mass of the polymers was analyzed by AF4 (Asymmetric- Flow Field Flow Fractionation). More detailed information is referred in Appendix I section I.2.

3.2. Basic Hydrolysis of PNVF

The poly (vinylamine), PVAm, was synthesized by basic hydrolysis of polyNVF polymers [3] as described in this chapter section 3.1. A solution of polyNVF was added to a jacketed reactor and purged for 30 min under mild N_2 flow. Reactor temperature was increased to 70 ºC and a solution of sodium hydroxide (NaOH), in a ratio relation $\frac{NaOH}{PNVF} = 2\ (mol)$, was injected to start the hydrolysis that was carried out for 6 hours. During the hydrolysis, at intervals of 30, 60, 120, 240 and 360 min an aliquot of 40 cm^3 approximately was taken from the flask and neutralized to pH=6 using HCl (1N) in order to stop further hydrolysis. At the end the solution was dialyzed to get rid of the sodium formate formed during the hydrolysis reaction. The solution was left in membranes (4 Spectra/Por® Dialysis membrane MWCO: 12-14 000) which was placed in a recipient filed with water during one month. During this time, the ultrapure water (Millipore) was changed every day and its conductivity was measured. When the conductivity reaches one value close to zero (formic acid disappeared), the solution was ready to use in the polymerization reactions. Other methods (rotavapor and lyophilizer) were tested to eliminate the sub product but without success.

The aqueous solution obtained was directly used in the surfactant free emulsion polymerizations of MMA.

3.2.1. PVAm Characterization

The kinetics of the hydrolysis reaction was analyzed by nuclear magnetic resonance spectroscopy, ^{1}H NMR, and it was confirmed that the amide groups (at 8.0-9.0 ppm) fully disappeared after 6 hour of reaction. A Bruker DRX-500 spectrometer 400 MHz was used and the samples were dissolved in deuterium oxide (D_2O).

As an example, the evolution of the ^{1}H NMR spectrum during the reaction is show in Figure 15 the NMR characterization of PNVF. Depletion of the protons signals at 7.0-8.0 ppm on 360 min confirms the absence of free monomer and therefore total conversion was achieved. After hydrolysis, to remove byproducts (sodium formate salt) the final samples (PVAm) were dialyzed. In Figure 15 (after dialysis), it is possible to see through ^{1}H NMR spectrum that the peaks at 8.5 ppm disappeared. The ^{1}H NMR spectra for the others PVAm obtained, can be seen in Appendix I, section I.3.

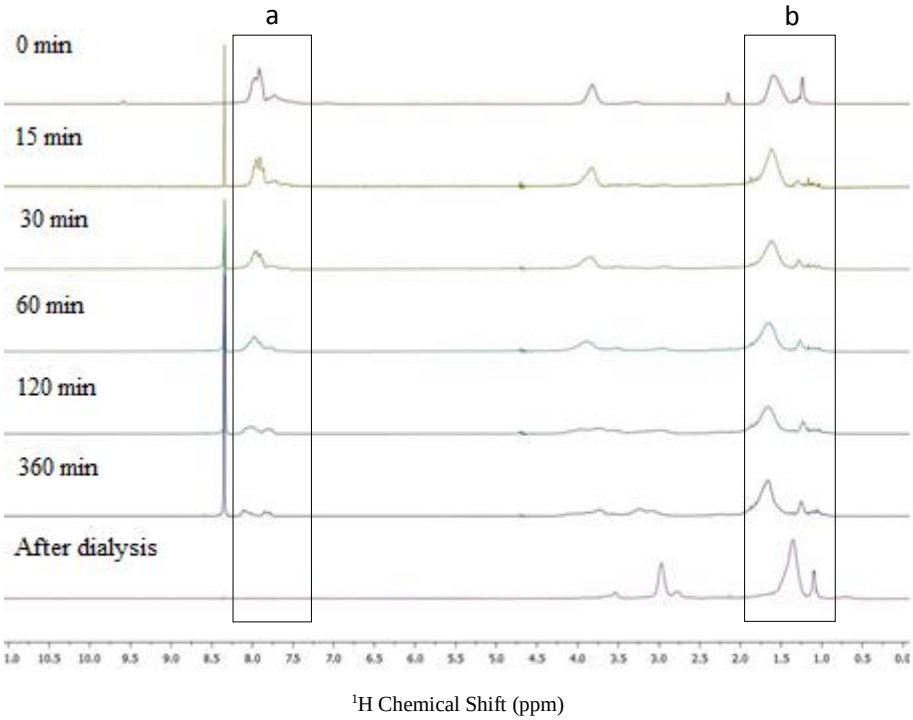

Figure 15. ^{1}H NMR spectra of PNVF2 polymer at different reaction times (0, 15, 30, 60, 120 and 360 min) and after dialysis.

The hydrolysis conversion was calculated using the following equation:

$$conversion\ (\%) = \left(1 - \frac{\left(\int \frac{a}{b}\right)_{generic\ time}}{\left(\int \frac{a}{b}\right)_{t=0}}\right) \times 100 \quad (2)$$

To perform the previous calculation, it was necessary to relate the ^{1}H NMR spectra of the polymer (polyNVF) at time zero (before hydrolysis), with the ^{1}H NMR spectra of the polymer, during the hydrolysis, at different times. Comparing the depletion peaks of the amide groups with the peaks of the -CH_2- in both spectra it was possible to calculate the conversion.

3.3. Surfactant-free emulsion polymerization

3.3.1. Material

Methyl methacrylate (MMA) (colorless liquid, Mw=100.12, density=0.936 g/cm^3, Aldrich) was purified by rotavapor before use (Buchi rotavapor® R-200). *Tert-Butyl* hydroperoxide (TBHP) (70% aqueous solution, colorless liquid, Mw=90.12, Aldrich), Potassium persulfate (KPS) (purity 99 %, solid, Mw=270.32, Aldrich), poly (vinylamine) was use as received. Poly (vinyl amine) was prepared as described in section 3.1.2. Distilled water was used throughout this work.

3.3.2. Procedure

This polymerization was carried out in a 150 ml jacketed reactor equipped with a turbine impeller rotating at 160 rpm and under a mild flow of N_2. In the first step, the PVAm and water were added to the reactor and mixed during 15 min at room temperature. After 15 min the reactor was heated until 80 ºC, and purged with N_2. When the reaction temperature was reached, the monomer (MMA) was injected. The polymerization started by adding an aqueous solution of initiator (TBHP or KPS). Polymerizations were carried out using PVAm of different molar masses. Figure 16 shows the setup used to carry out this synthesis.

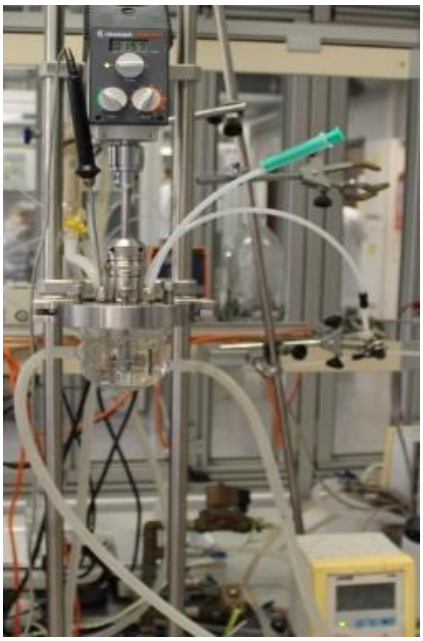

Figure 16. Experimental setup used in synthesis PMMA/PVAm particles.

Table 5. Formulations employed in the synthesis of PVAm: PMMA latex.

Run	PVAm: MMA (wt:wt)	Type of initiator	Initiator:PVAm[a] (mol:mol)
R1	1:4	TBHP	1:1
R2	1:4	TBHP	1:50
R3	1:4	TBHP	1:100
R4	1:4	TBHP	1:200
R5	1:4	TBHP	1:1
R6	1:4	TBHP	1:50
R7	1:4	TBHP	1:100
R8	1/4	TBHP	1:50
R9	1:4	TBHP	1:100
R10	1:4	TBHP	1:1
R11	1:4	TBHP	1:100
R12	1:4	KPS	1:100

[(a)] The molar ratio was calculated with respect of PVAm units, more detailed information is referred in Appendix I section I.4.

3.3.3. Characterization of the PMMA/PVAm particles.

- ✓ **Conversion**

After polymerization, the solid content of the latexes was measured gravimetrically. The polymer conversion, which refers to the weight percentage of polymerized MMA in particles based on the total weight of monomer added, was calculated as follows:

$$\text{monomer conversion}(\%) = \frac{W_s - (W_p + W_i)}{W_t} \times 100 \quad (3)$$

Where, W_s is the weight of total solid in dispersion, W_p is the weight of the water soluble polymer, W_i is the weight of the initiator and W_t is the total weight of the monomer.

- ✓ **Grafting efficiency**

The graft copolymers and PMMA homopolymers were isolated from the resulting polymers by Soxhlet extraction with tetrahydrofuran (THF) during 24 hours. The graft copolymers were then collected in the thimble and the homo-PMMA was dissolved in THF and collected in the round bottom flask. Figure 17 shows the scheme of Soxhlet extraction. More detailed information is referred in Appendix I section I.5.

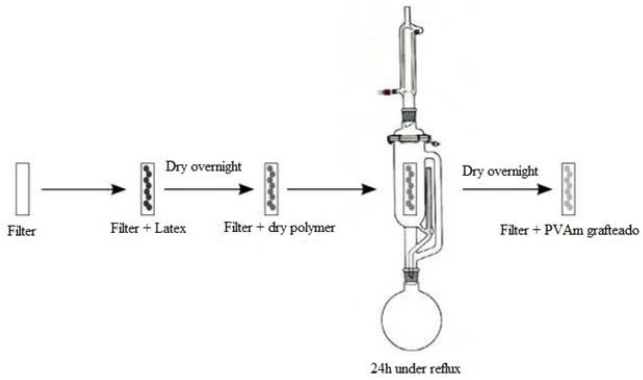

Figure 17. Scheme of Soxhlet extraction method for grafting efficiency measurement.[4]

Grafting efficiency was calculated using the following equation:

$$GE\ (\%) = \frac{Weight\ of\ grafted\ PMMA}{Weight\ of\ total\ polymerized\ MMA} \times 100 \quad (4)$$

Where:

$$weight\ of\ grafted\ PMMA = \ weight\ \ dry\ samples\ after\ soxhlet - weight\ of\ PVAm\ in\ sample$$

- ✓ **Composition of PMMA/PVAm particles**

FT-IR (Fourier transform infrared Spectroscopy) spectra were recorded on Alpha FT- IR spectrometer. In order to do the analysis, the sample was dried in the oven. Afterwards the sample was milled and turned into a powder. Then the powder was placed on top of the diamond and the measurement was made.

- ✓ **Particle size and size distribution of PMMA/PVAm particles**

Polymer particle sizes were measured by dynamic light scattering (DLS) using Malvern Zetasizer Nano ZS (laser: 4 mw, He-Ne, λ=633 nm, angle 173º). The equipment determines the particle size by measuring the rate of fluctuations in light intensity scattered by particles to Brownian motion. More detailed information is referred in Appendix I section I.6.

- ✓ **Morphologies of PMMA/PVAm particles**

The morphology of the latex particles was also studied by means of transmission electron microscopy (TEM Tecnai ^{TM} G^2 20 Twin device at 200 kV (FEI Electron Microscopes)). Each sample was prepared by wetting a carbon-coated grid a small drop of dilute particle dispersion. The dried particles were cryosectioned with a Reichert-Jung Ultracut E cryoultramicrotome at -70 ºC with a Diatome 45º diamond knife and the observations were made with a Philips CM10 transmission electron microscope operated at 80 kV without staining.[4]

- ✓ **PMMA molecular weight**

The molecular weight of the PMMA (obtained by Soxhlet extraction) was determined by size exclusion Chromatography/Gel Permeation Chromatography (SEC/GPC). At first, the samples taken out from the soxhlet were dried and dissolved in pure THF to achieve a concentration of about 0.1 g/ml, furthermore before injection into SEC instrument the samples were filtered in order to avoid the presence of any impurity. More detailed information is referred in Appendix I section I.7.

3.2. Reference list

[1] Ernst, R. R,; Bodenhausen, G.; Wokaun, A.," Principles of Nuclear Magnetic Resonance in One and Two dimensions, *Oxford University Press*, New York **2004**

[2] Gu, L.; Zhu, S.; Hrymak, A. N. Acidic and basic hydrolysis of poly (vinylformamide). *Journal of Applied Polymers Science* **2002**, 86 (13), 3412-3419.

[3] Rodríguez, M. M. "Waterborne Polymers based on Sunflower oil fatty acids"University of the Basque Country, Donostia-San Sebastian, **2013**.

[4] Bonnefond, A., Micusík, M.; Paulis, M.; Leiza, J. R; Teixeira. R. F. A.; Bon, S. A. F., "Morphology and properties of waterborne adhesives made from hybrid polyacrylic/montmorillonite clay colloidal dispersions showing improved tack and shear resistance", *Colloid Polym Sci,* **2013,** 291:167-180.

Chapter 4

Experimental Results and discussion

4.1. Aqueous solution polymerization of NVF

In order to obtain PNVF with different molecular weights, reactions in different conditions were performed. The kinetics of the monomer conversion was analyzed in all the polymerizations by taken samples over time. Figure 18 represents the conversion of the polymer over time for reaction PNVF2 and PNVF3.

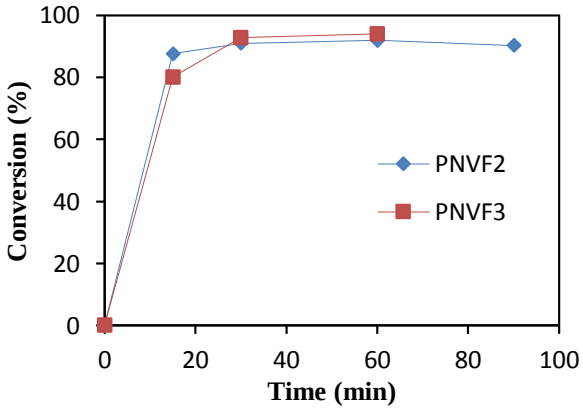

Figure 18. Evolution of the polymer conversion for PNVF2 and PNVF3 during the reaction time.

The weight average molecular weight (Mw), number average molecular weight (Mn) and polidispersity index (PDI) for the different polymers obtained was analyzed by AF4, as described in chapter 3. Table 6 shows the results obtained for the different polymers. The graphics obtained by AF4 are presented in Appendix II, section II.1.

Table 6. Results obtained in the different synthesis of the polyNVF.

Name of the polyNVF	Final pH	Final conversion (%)	Mw (Da)	Mn (Da)	PDI
PNVF1	6	100	105 000	69 100	1.5
PNVF2	6.5	90	47 500	34 600	1.3
PNVF3	6.2	94	14 800	9900	1.5
PNVF4	6.5	84	13 800	8700	1.6

As it can be seen the molar masses increases as the monomer concentration increases. This result was expected taking into account that the polymerization was carried out in solution. At constant temperature, increasing the monomer concentration implies the increasing of the ratio (k_p [M]/k_t [I] $^{1/2}$) that controls the kinetic chain length. Therefore the effect of the monomer concentration on the molar masses fulfilled what it can be expected in solution polymerization.[1] Analyzing Table 4 and Table 6, increasing the reaction temperature notably decreased the molar masses. This result indicates that the polymerization temperature is also a key factor affecting the Mw of the polymer produced, as was expected.[1, 2]

4.2. Basic hydrolysis of NVF

The polymers (PNVF) which have been previously produced were converted to PVAm through basic hydrolyses and slight-yellow products were achieved. Figure 19 show the aspect of the final product obtained through the basic hydrolysis.

Figure 19. Aspect of the final product (PVAm) obtained through the basic hydrolysis.

The conversion was calculated through the ^{1}H NMR spectrum, using Equation 2 in chapter 3. Figure 20 shows the evolution of the hydrolysis conversion during the reaction time for the different reactions (PNVF1, PNVF2 and PNVF3). For the hydrolysis of PNVF4 polymer, it was not possible to take samples over time. Table 7 shows the final monomer conversion for PNVF1, PNVF2, PNVF3 and PNVF4.

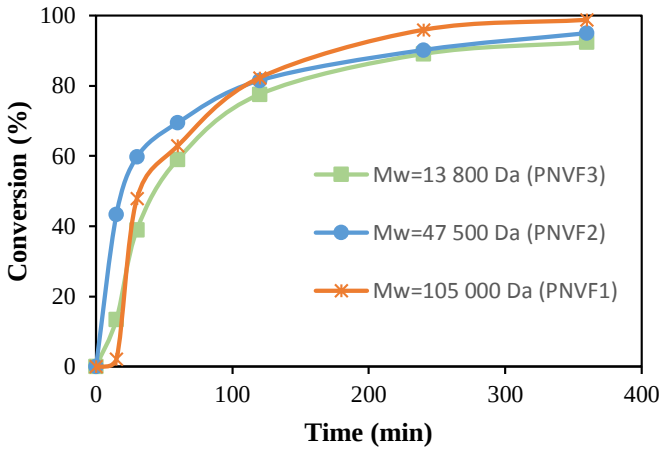

Figure 20. Evolution of the basic hydrolysis conversion for the different polymers (PNVF1, PNVF2 and PNVF3).

Figure 20 show that the kinetics of hydrolysis are similar for all the cases. Table 7 shows the results of conversion and solids content of the different hydrolyses carried out. The polymer with the highest conversion was PNVF1.

Table 7. Experimental results of the final hydrolysis conversion (%) for the different polymers.

Name of the polymer	Mw (Da)	Final conversion (%)	Solids Contents (%)
PNVF1	105 000	99	1.04
PNVF2	47 500	95	1.23
PNVF3	14 800	93	0.3
PNVF4	13 800	98	1.6

(a) The percentage of solids contents was different for each polymer because, during dialysis the samples were diluted in a random way which was not possible to control.

Four polymers with different molecular weight were synthesized, nevertheless in the last process (surfactant-free emulsion polymerization) only three of them were used. The reason for that choice was that PNVF3 and PNVF4 had almost the same Mw, so as PNVF3 has lower percentage of solids contents, PNVF4 was used.

4.3. Surfactant-free emulsion polymerization of MMA stabilized by PVAm

Pei Li et al.[4, 5] pioneered the route to synthesize core-shell polymer nanospheres using water soluble polymers containing amino groups in absence of any surfactant. The polymerization is based on the reaction between alkyl hydroperoxides and the amino groups of the water soluble polymer PVAm, in water in the presence of a dispersed hydrophobic monomer, MMA. During the reaction, the hydroperoxides initially interact with amino groups on the polymer backbone, generating macromolecular radicals might also abstract hydrogen atoms from the water soluble polymers, thus generating macromolecular radicals that could also initiate the graft copolymerization.[6] The amphiphilic PVAm-g-PMMA graft copolymers generated in situ act like polymeric surfactants, and self-assemble to form micelle-like microdomains. The micellar domains subsequently promote the emulsion polymerization of MMA. Stable particles were then produced in the absence of surfactant. Thus the water- soluble polymer provides not only reactive points such as amino groups for initiation, but also the electrostatic and steric stabilization (Figure 21).[7]

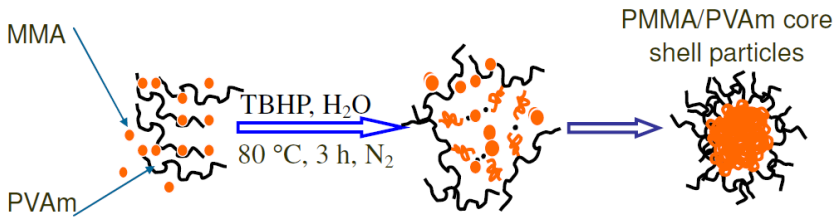

Figure 21. Scheme of the graft copolymerization of MMA from PVAm.[6]

Table 8 presents the experiments carried out in this work following this approach PVAm polymers synthesized by hydrolysis of PNVF were used. PVA's with three different molecular weights (13 800, 47 500 and 105 000 Da) were used. The ratios TBHP: PVAm and PVAm: MMA, pH and type of initiator were varied in order to see the effect on the final conversion and particle sizes.

Table 8. Different polymerization conditions for the synthesis of MMA by surfactant free emulsion polymerization.

Run	PVAm molecular weight (Da)	PVAm:MMA (wt:wt)	TBHP:PVAm (mol:mol)	pH[a]	Final monomer conversion (%)	Average diameter (nm)
R1	105 000	1:4	1:1	9.5	17	107
R2	105 000	1:4	1:50	9.4	58	437
R3	105 000	1:4	1:100	9.4	81	829
R4	105 000	1:4	1:200	9.6	72	518
R5	47 500	1:4	1:1	9.5	35	90
R6	47 500	1:4	1:50	9.6	71	235
R7	47 500	1:4	1:100	9.4	52	224
R8	13800	1:4	1:50	9.4	83	146
R9	13800	1:4	1:100	9.5	82	383
R10	13800	1:4	1:1	9.5	36	91
R11	105 000	1:4	1:100	4.7	70	759
R12[b]	105 000	1:4	1:100	9.3	48	152

(a) pH of the dispersion after polymerization.
(b) Run with a different Initiator: KPS

All reactions were performed during four hours, the exception were R2, R3 and R4. These reactions had a longer reaction time (6 hours), after the initial 4 hours of reaction; a new shot of initiator was added to the reactions R2 and R3 (1/4 with respect to the initial amount) followed by 2 hours of cooking. For the reaction R4, after 4 hours of reaction 1/4 of initial amount of initiator and PVAm were also added. This test was done with the objective of increasing conversions that were not complete in the first step. However these attempts were not successful, illustrate in Figure 25. In Figure 22 is presented the final aspect of a latex.

Figure 22. Final aspect of a latex (R3).

4.3.1. Reaction Reproducibility

To check the reproducibility of the process, two reactions (R3 and R7) were replicated. For these experiments the conversion, pH and evolution of the particle size during the reaction time was studied. The results are shown in the Figure 23 for two replicated experiments of reaction R3 and in Figure 24 for experiment R7.

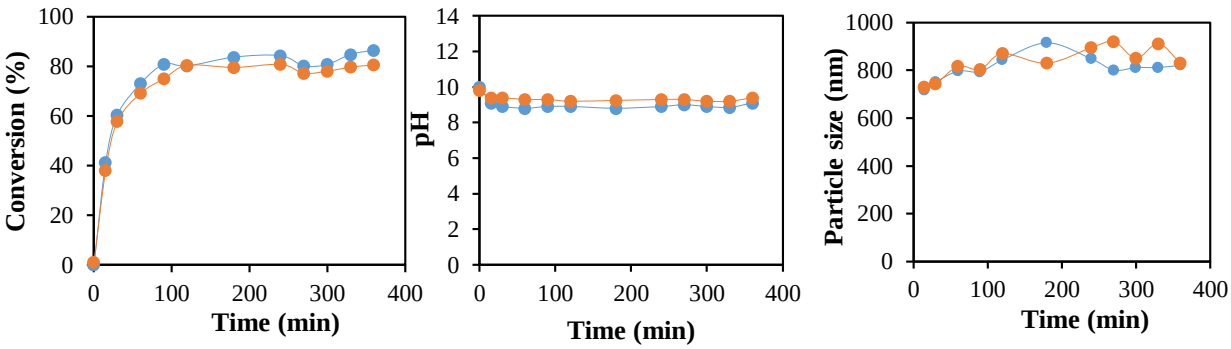

Figure 23. Representations of the conversion, pH and particle size during the reaction time for the Run R3.

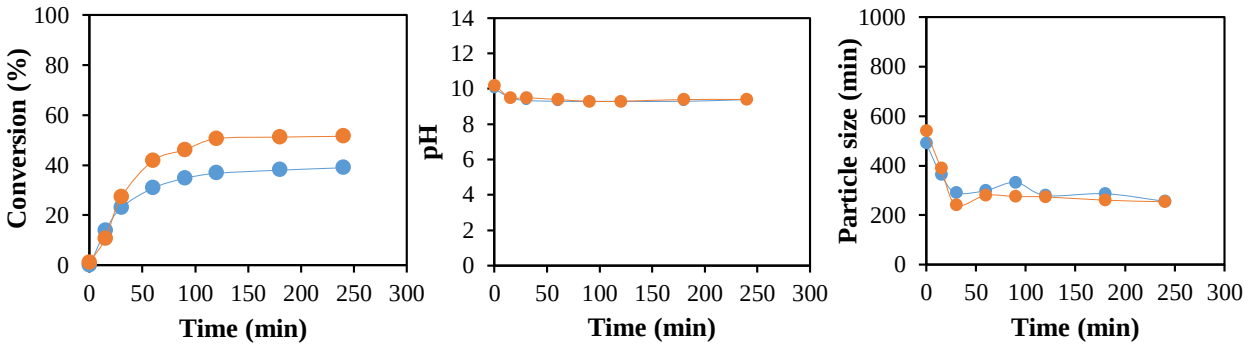

Figure 24. Representations of the conversion, pH and particle size during the reaction time for the Run R7.

Analyzing the graphs in figure 23 and 24, it is possible to conclude that both reactions R3 and R7 are reproducible. A slight difference was obtained for reaction R7

4.3.2. Effect of TBHP concentration

The graft copolymerization of MMA from PVAm was induced by a small amount of TBHP which is a water-soluble initiator. TBHP molecule form redox pairs with the amino groups, generating amino and t-Butoxy radicals concurrently. The amino radicals can initiate the graft copolymerization of MMA from PVAm to generate PVAm-graft-PMMA amphiphilic copolymers, while the t-Butoxy radical can initiate the homopolymerization of MMA.[5-7]

To investigate the effect of TBHP concentration on the polymerization of MMA from PVAm, TBHP: PVAm molar ratio ranging from 1:1 to 1:200 mol:mol was used in a series of experiments. The conditions and results used in these experiments are present in Table 8. The following figures (25, 26 and 27) show the effect of TBHP concentration on the results of conversion, pH and particle size distribution in the surfactant-free emulsion polymerization for reactions stabilized with three different PVAm polymers.

Results in Figures 25, 26, 27 and data in Table 8 shows that the pH of the reaction mixture dropped from 11 to 9.5 after polymerization. This result was due to the hydrolysis of monomer under basic conditions and the conversion of primary amine groups to neutral covalent C-N bond of the amine group to MMA monomer.[7]

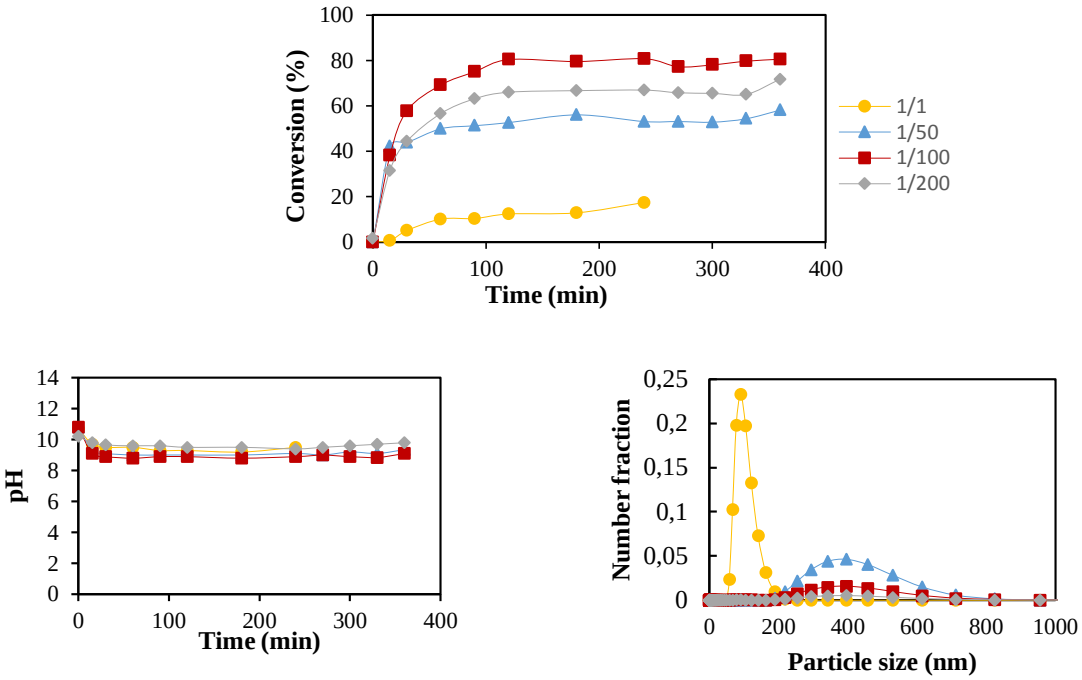

Figure 25. Time evolution of the conversion, pH and particle size distribution for experiments carried out with different molar ratios of TBHP:PVAm, using PVAm with Mw= 105 000 Da (PNVF1).

The monomer conversion fluctuated with the TBHP molar rations varied from 1:1 to 1:200 mol:mol, indicating that TBHP concentration had influence in this range.

Analyzing Figure 25, when the molar ratio of TBHP:PVAm decreased from 1:1 to 1:100, the conversion of monomer increased from 17% to 81 % approximately. For molar ratio of TBHP: PVAm =1:200, the conversion of monomer decreased to 72%, i.e. the maximum of monomer conversion was achieved for the molar ration of 1:100. Also it can be seen in that after 4 hours when a new shot of initiator was performed, monomer conversion remained constant.

Regarding the particle size, this parameter was small when the molar ratio of the TBHP:PVAm was 1:1, which might be due to the low monomer conversion. When the molar ratio of the TBHP:PVAm decreased from 1:1 to 1:200, the average diameter of particle increased from 107 to 518 nm and the particle size distribution became wider. Although, for the molar ratio of 1:200 the final monomer conversion decreased and the average of the particle size diameter increased.

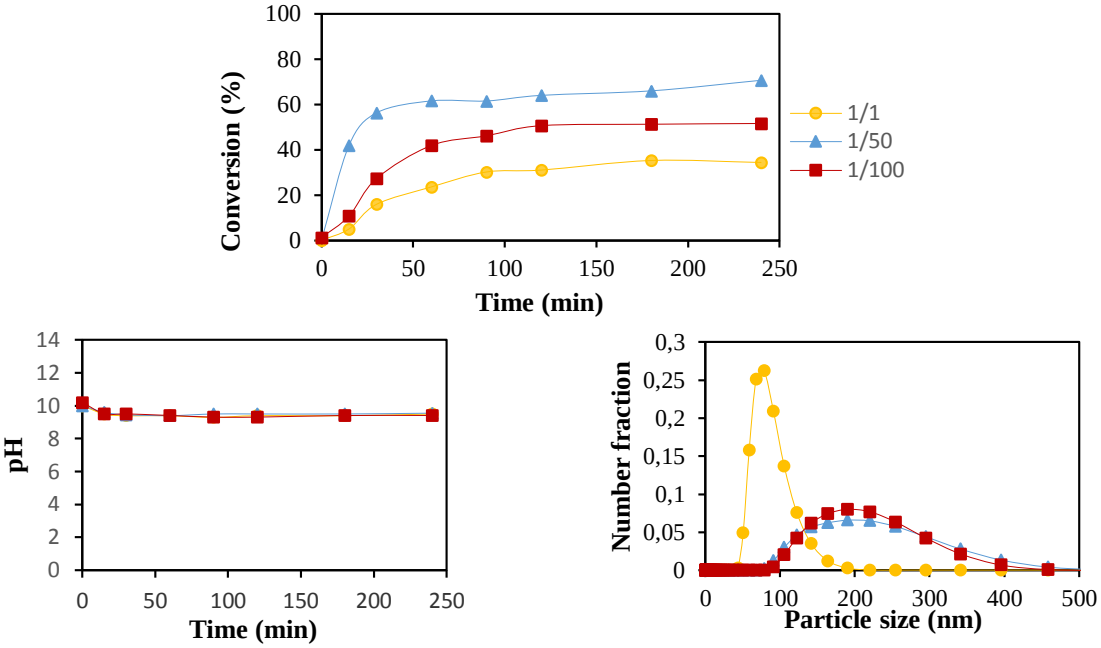

Figure 26. Time evolution of the conversion, pH and particle size distribution for experiments carried out with different molar ratios of TBHP:PVAm, using PVAm with Mw= 47 500 Da (PNVF2).

Figure 26 shows that the monomer conversion increased with decreasing the molar ratio of TBHP:PVAm, achieving the optimum, and then decreased again. The optimum molar ratio of TBHP:PVAm was found to be 1:50, when the highest conversion (71%) was reached. The average diameter of the particles varies with monomer conversion and size distribution of the particles became wider at higher conversions.

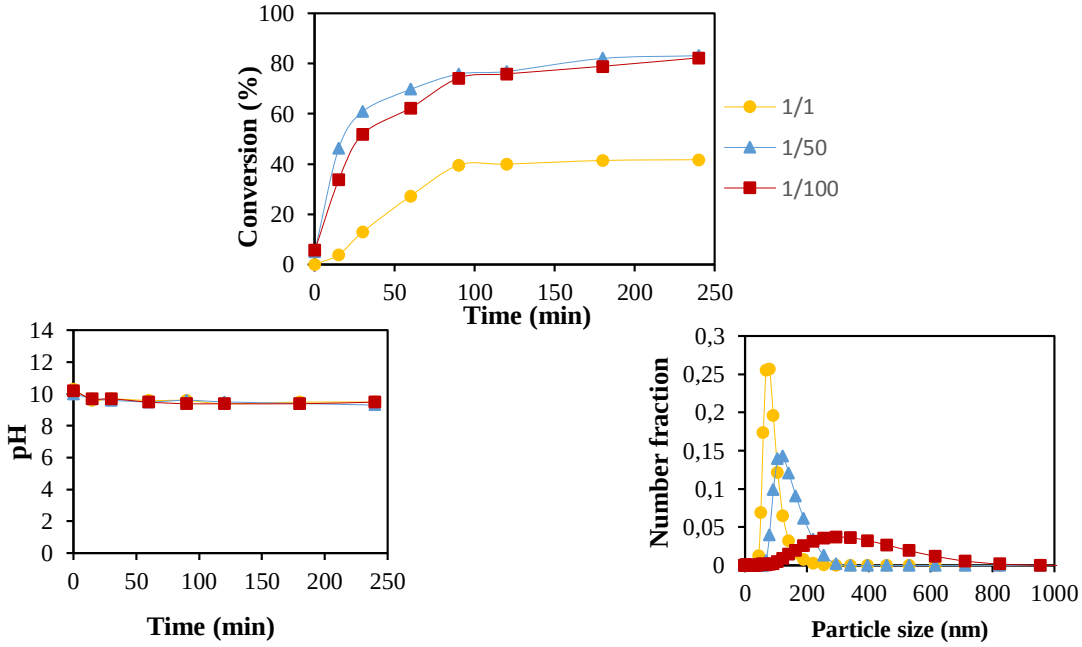

Figure 27. Time evolution of the conversion, pH and particle size distribution for experiments carried out with different molar ratios of TBHP:PVAm, using PVAm with Mw= 13 800 Da (PNVF4).

In Figure 27 and Table 8, the monomer conversion also increased when the molar ratio of the TBHP:PVAm decreased, but in this case it wasn't possible to distinguish the optimum molar ratio.

The monomer conversion for the molar ratio TBHP:PVAm =1:50 (83 %) was similar comparing to the molar ratio TBHP:PVAm =1:100 (82 %). The evolution of the monomer conversions of these reactions was almost the same.

The behavior of the particle size distribution was very different. The average diameter of particles increased when the molar ratio of the TBHP:PVAm decreased and the distribution of particle size became wider. The increase of particle size and increase of the monomer conversion indicated a decrease of the number of particles in the reaction system.

The effect of TBHP:PVAm molar ratio on the particle morphology was also investigated. Figure 28 shows that some particles synthesized with Mw=105 000 Da using different TBHP:PVAm molar ratio had similar surface morphology with a rough surface, indicating that TBHP:PVAm had little effect on the surface morphology of the particles. In other words, the key factor that affected the surface morphology of the particle was not the molar ratio TBHP:PVAm.

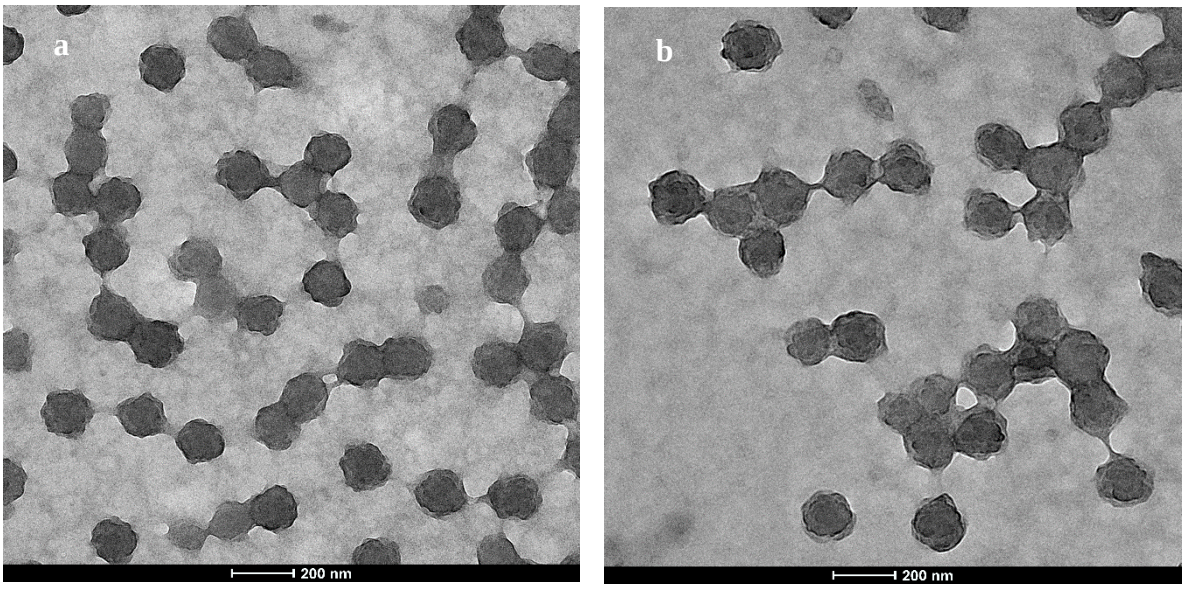

Figure 28. TEM micrographs of PMMA/PVAm particles produced by surfactant free emulsion polymerization of MMA stabilized by PVAm with different TBHP:PVAm molar ratio (mol:mol): a) 1:50; b) 1:100.

4.3.3. The effect of the molecular weight of PVAm

In order to obtain stable latexes, an important criterion must be satisfied: the particles must be stabilized in water via electrostatic or steric interaction or a combination of both. For the PMMA/PVAm particles, almost all the amino groups are in the form or primary amine at pH 12, thus there is a little electrostatic repulsion between the particles. Therefore, the particles stability in water mainly relies on the steric stabilization of PVAm chains which is strongly dependent on the molecular weight and architecture of the PVAm. The molecular weight of PVAm might influence the particles in two aspects: 1) the increase in molecular weight of PVAm can enhance the steric effect, thus improving the stability of the particles; 2) The molecular weight may change the shell thickness of the particles, thus varying the surface morphology of the particles.[7]

To investigate the effect of molecular weight on the surfactant-free emulsion polymerization of MMA stabilized by PVAm, three PVAm with different molecular weights were tested, by varying the molar ratio of initiator, as described in Table 8.

Figures 29, 30 and 31 present the results for the monomer conversion during the reaction time and the particle size distribution for three different molecular weights, for the molar ratio of TBHP: PVAm 1:1, 1:50 and 1:100 mol: mol, respectively.

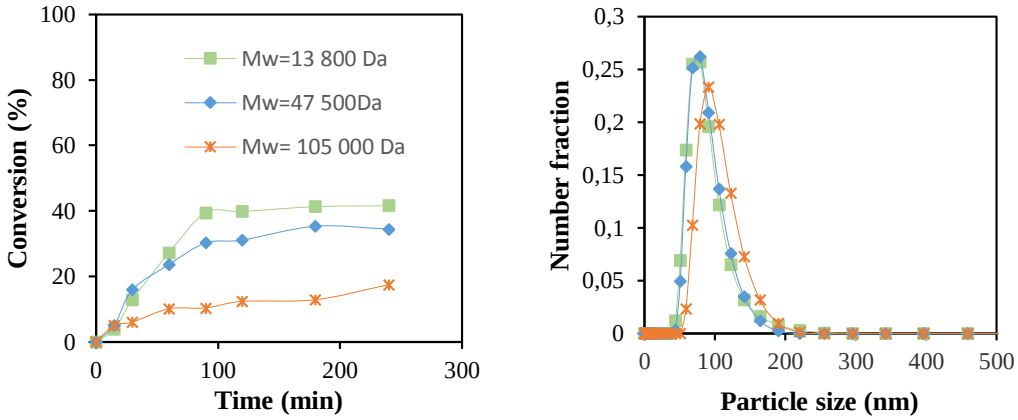

Figure 29. Time evolution of the conversion and the particle size distribution for experiments carried out with TBHP:PVAm =1:1 mol:mol.

Analyzing Figure 29 it can be seen that as the molecular weight of PVAm increased the monomer conversion decreased and the particle size distribution were narrower. The average of particle size diameter was small and very similar, increasing slightly with the increase of the molecular weight, from 90 to 107 nm

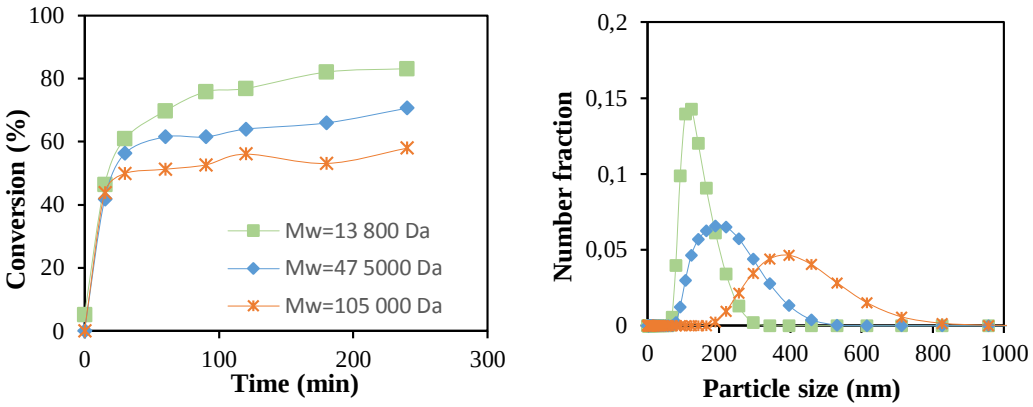

Figure 30. Time evolution of the conversion and the particle size distribution for experiments carried out with TBHP:PVAm =1:50 mol:mol.

For the molar ratio of TBHP:PVAm=1:50 mol:mol (Figure 30), the same behavior happened, as the molecular weight of PVAm decreased, the monomer conversion increased. Also, increasing the molecular weight, particle size distributions became wider and the average diameter increased from 146 to 437 nm.

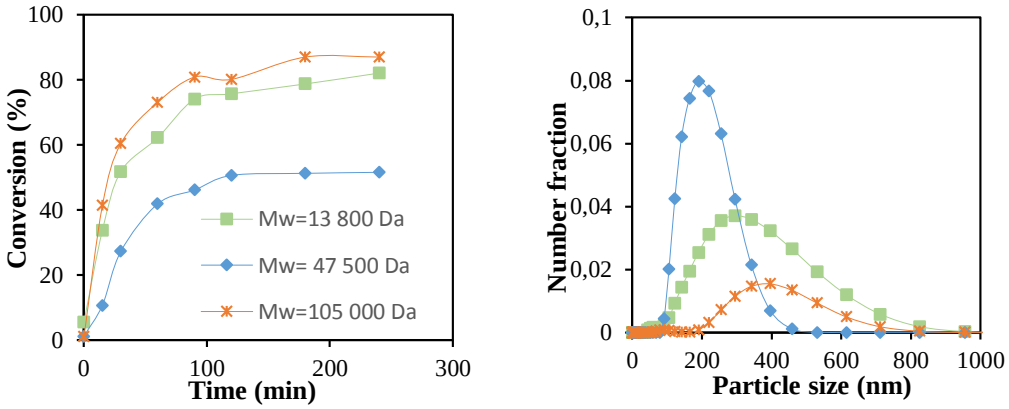

Figure 31. Time evolution of the conversion and the particle size distributions for experiments carried out with TBHP:PVAm =1:100 mol:mol.

In the case of TBHP:PVAm = 1:100 mol: mol ratio, a different behavior was observed compared to the cases studied previously. In Figure 31, it can be seen that the highest monomer conversion corresponded to Mw= 105 000 Da and the molecular weight that had lower conversion was Mw= 47 500 Da. Regarding the average diameter of the particle, it was observed that the diameter of polymer particles for the reaction carried out with the PVAm of Mw= 105 000 Da was equal to 458 nm, and when the molecular weight

decreased to 47 500 Da the average diameter also decreased (224 nm). However the diameter of particles measured for the reaction carried out with the lowest molecular weight PVAm (383 nm) was larger than the diameter of particles measured for the reaction carried out with the intermediate molecular weight PVAm. This was ascribed to the low conversion obtained for the intermediate molecular weight PVAm.

Those results can be explained by the following way: Taking into consideration the mechanism presented in Chapter 2 for this reaction, it can be said that in the presence of the lowest molecular weight PVAm, the aggregated domains where the MMA polymerization takes place were formed earlier compared to the cases when higher molecular weights PVAm were employed. This was due to the fact that as the hydrophilic part of the copolymers is smaller, the copolymer will need less monomer units to aggregate and form micelles-like domains. Also, a higher number of hydrophobic-hydrophilic copolymers were formed which will act as particles stabilizers. Thus in this case the system acts as if a higher amount of surfactant was employed in the reaction. Therefore, the diameter of particles is smaller and higher number of particles are formed. Thus the reactions kinetics is faster and lead to higher conversions than for the reaction carried out with higher molecular weights PVAm. This might explain the smaller sizes and higher conversions obtained for the reactions carried out with the lowest molecular weight PVAm compared to the two other ones. Nonetheless, the conversion obtained with high amounts of TBHP was lower than that with lower amounts of TBHP due to the termination reactions that occurred by entry of the large amount of hydroxyl radicals present in the aqueous phase to the polymerizing particles.

Such behavior became less pronounced as the amount of TBHP decreased because as the TBHP concentration decreased, a lower amount of copolymers was formed and then less micelles-like domains were obtained. Thus the diameter of particle obtained was larger. Nonetheless the conversion was higher because less termination reactions could occur by the entry of hydroxyl radicals present in the aqueous phase to the polymerizing particles.

After studying the monomer conversion, the average diameter of the particles and particle size distributions changing the molar ratio of TBHP: PVAm and the molecular weight of PVAm, the grafting efficiency, the morphologies of the PMMA/PVAm particles and the molecular weight of PMMA were also studied. The grafting efficiency was calculated by the equation 4, in chapter 3. The following Table presents the results of the grafting efficiency and molecular weights of PMMA.

The molecular weight values of PMMA for all the samples was high. However for low percentage of grafting efficiency, these values were lower. In Appendix II, section II.2., the graphs of the molecular weights distributions for PMMA are represented.

Table 9. Conditions and results of grafting efficiency and PMMA molecular weight on the surfactant free emulsion polymerization of MMA stabilized by PVAm.

Run	Molecular weight (Da)	TBHP:PVAm (mol:mol)	Grafting efficiency (%)	PMMA molecular weight (Da)
R1	105 000	1:1	18	17919
R2	105 000	1:50	50	436453
R3	105 000	1:100	59	334545
R4	105 000	1:200	62	469175
R5	47 500	1:1	18	26044
R6	47 500	1:50	53	256995
R7	47 500	1:100	60	164338
R8	13 800	1:100	40	269573
R9	13 800	1:50	43	213824
R10	13 800	1:1	19	19144

Figure 32 compares the values of grafting efficiency for all the experiments for three different molecular weights of PVAm and different molar ratios of TBHP:PVAm.

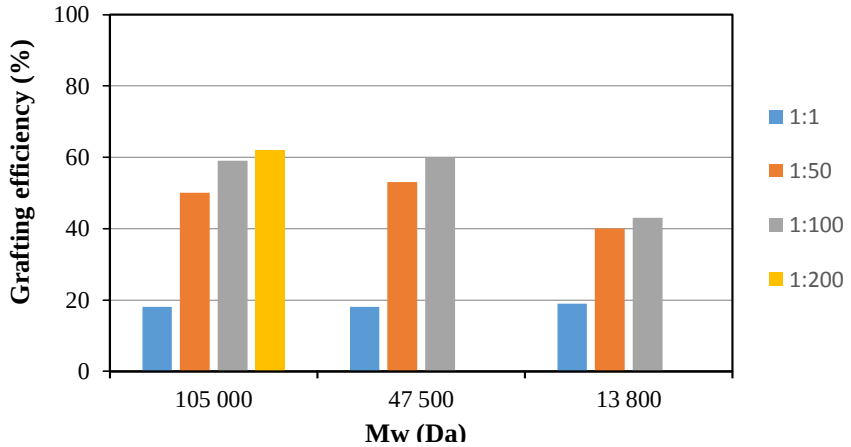

Figure 32. Representation of the grafting efficiency for the different molecular weights and the different molar ratio of TBHP:PVAm.

Analyzing the Figure 32, it can be seen that the grafting efficiency and molecular weight of PMMA increased significantly with the decrease of the molar ratio

TBHP:PVAm for three different molecular weights. This effect might be due to the fact that a higher TBHP: PVAm molar ratio would result in higher t-butoxy and amino radicals concentrations through the redox reaction of TBHP with the amino groups from PVAm chains. This would increase both the number of grafting points from PVAm chains due to the higher number of amino radicals and the rate of homopolymerization of MMA by presence of t-butoxy radicals in the aqueous phase. Comparing the grafting efficiency for three different molecular weights, it can be seen that the grafting efficiency varied with the molecular weight of PVAm. The values of grafting efficiency of the PVAm for molecular weights of 105 000 Da and 47 500 Da were similar, but for Mw =13 800 Da the values of grafting efficiency decreased significantly. Grafted PMMA chains are formed by the reaction of MMA monomer with the amino radicals formed by the reaction between TBHP and the amines from PVAm chains. The amphiphilic graft copolymers generated are able to form micelles wherein the polymerization of MMA takes place. When low molecular weight polivinylamines were employed, the amount of grafted PMMA necessary to form micelles was lower because with very low amounts of grafted PMMA the copolymer became hydrophobic enough to aggregate. Thus the grafting efficiency was lower in this case.

Figure 33 shows the morphologies of the PVAm: PMMA particles obtained using PVAm with different molecular weights. Even of at first sight it seems that these particles had similar morphologies, longer hair-like shell was observed when high molecular weight PVAm was employed. Thus it can be said that the molecular weight of PVAm affected to some extend the morphology of the particles.

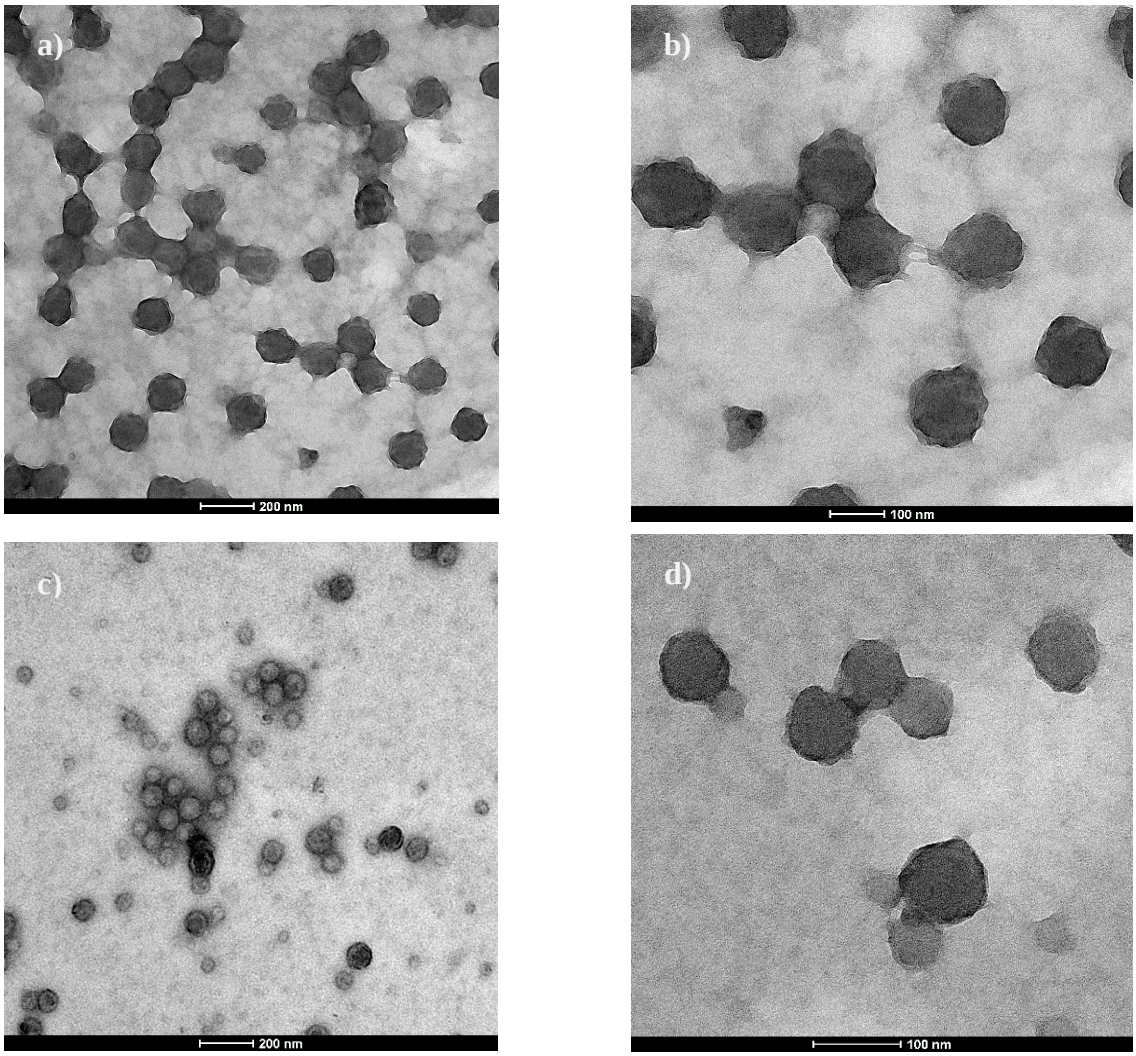

Figure 33. TEM micrographs of PMMA/PVAm particles prepared with two different molecular weight of PVAm a) and b) Mw=105 000 Da; c) and d) Mw= 47 500 Da.

4.3.4. The effect of reaction pH

PVAm is a weak cationic polyelectrolyte, and its charge density can be varied by pH from fully ionized (pH<3) to completely neutral (pH >10)[8] Kirwan[9] observed that the PVAm experienced a conformational transition from coil to globule during the change of solution pH from acidic to basic condition. At low pH where PVAm is fully ionized (pH<3), it exists in an extended coil conformation. While at high pH (pH>10), the polyelectrolyte is completely de-protonated and has a globular conformation[7], as seen in Figure 34.

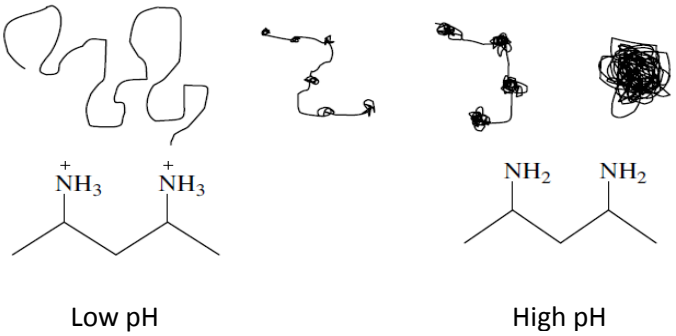

Figure 34. Representation of the extended coil-to-globular conformational transition for linear flexible poly (vinyl amine).[8]

Since the ionization degree of amine groups depends on the solution pH, it is anticipated that the pH of the reaction medium may strongly affect the polymerization and particle formation due to the differences in available amine groups and solubility of the resulting PVAm.[7] Therefore, the effect of the reaction pH on monomer conversion particle size distribution, grafting efficiency, morphology of the particles PMMA/PVAm and the molecular weight of PMMA was studied on the surfactant free emulsion polymerization of MMA stabilized by PVAm. The reaction pH was the pH of the PVAm dispersion.

This study was only done for the R3 reaction, the PVAm obtained by basic hydrolysis, was first dissolved in distillated water and the pH of solution was adjusted to 4.7 using a 1N HCl solution. The PVAm solution was treated under the same conditions as others reactions; the experimental procedure is described in chapter 3.

The following figure compares the results of the monomer conversion and the particle size distribution of reactions under the same conditions, but at different pH (acidic and basic).

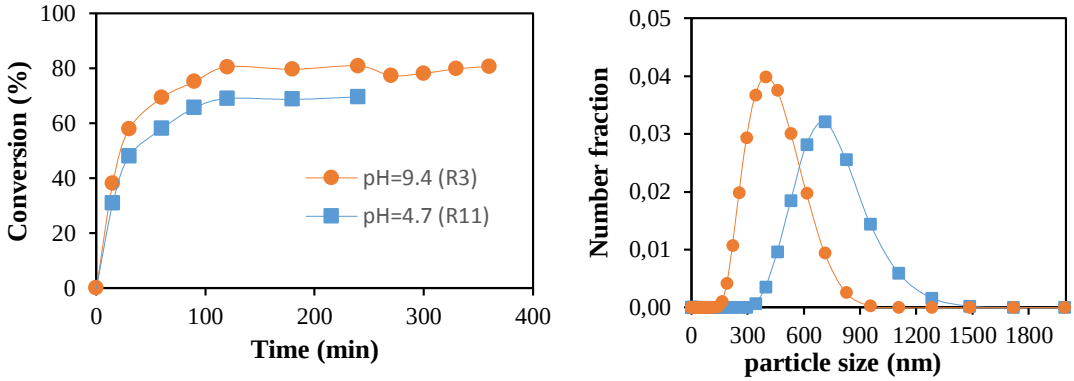

Figure 35. Comparison the results of conversion and number particle size distribution of the reactions SF23 and SF32.

The results in Figure 35 and in Table 8 indicate that the monomer conversion increased when the pH of the reaction increased. It had been observed that the number of deprotonated NH_2 groups increased with the increase of pH. Since primary amine groups are highly reactive electron-donating groups towards the redox reaction with alkyl hydroperoxide, the reactivity of PVAm thus is higher at higher pH.

Also the particle size increased with the decrease of the reaction pH. At lower pH (4.7), particles with an average diameter of 759 nm were generated and at higher pH (9.4) the particles had an average diameter of 459 nm. The increase of particle size at pH=4.7 can be attributed to the protonation of amine groups, leading to an expansion of the PVAm shell layer due to intramolecular charge repulsion.

Table 10 present the conditions and results of grafting efficiency for reactions R3 and R11.

Table 10. Conditions and results of grafting efficiency and PMMA molecular weight on the surfactant free emulsion polymerization of MMA stabilized by PVAm.

Run	Final pH	GE (%)	PMMA molecular weight (Da)
R3	9.4	59	334545
R11	4.7	2	190561

Figure 36, illustrates the percentage of grafting efficiency (GE %) as a function of reaction pH. As it can be seen the grafting efficiency rose considerably as the reaction pH increased. This brings light on the process of the reaction at low pH. Because of the low

reactivity of NH_3^+ groups, the homopolymerization of MMA would be fast and the MMA precipitates might be stabilized by the PVAm chains adsorbed at the surface of the aggregates by H bonds. Another assumption is that the poly (methylmetacrylate) formed might have suffered hydrolysis in the acidic medium and the hydrolyzed groups acted as stabilizers of PMMA particles. Thus almost no interaction might occur between PVAm and PMMA chains.

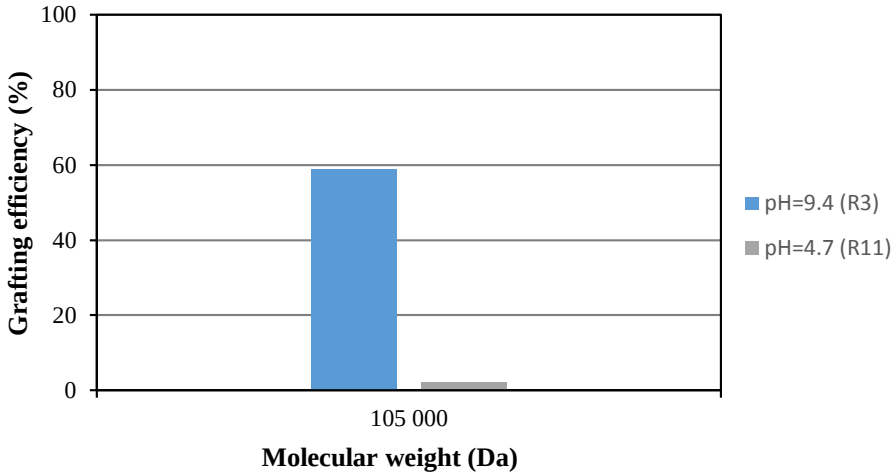

Figure 36. Representation of the grafting efficiency for reactions R3 and R11.

4.3.5. Effect of initiator type (KPS) in reaction

KPS is a water soluble anionic initiator and has been shown to provide sufficient stabilizing effect during the surfactant-free emulsion polymerization. This initiator in contact with amine groups forms the redox pairs.[10]

To investigate the effect of KPS initiator on the surfactant-free emulsion polymerization of MMA stabilized by PVAm, the monomer conversion, particle size and particle size distribution, grafting efficiency and morphologies of the particles were studied. Therefore, R12 reaction was carried out changing the initiator from TBHP to KPS, the reaction conditions are presented in Table 8. Figure 37, shows the comparison of the results regarding the monomer conversion and particle size distribution based,

under the same conditions, for the reaction R3 when TBHP was used and reaction R12 using KPS.

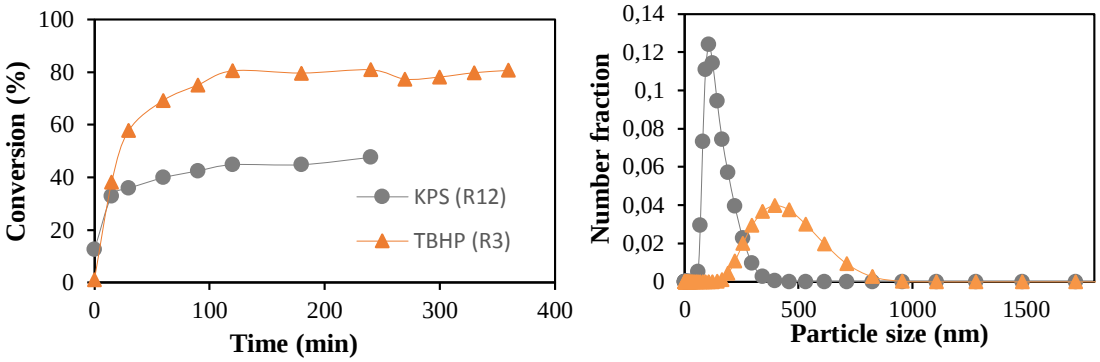

Figure 37. Comparison the results of conversion and particle size distribution based on number fraction of the reactions R3 and R12.

Analyzing Figure 37 and Table 8, it can be seen that for the same molar ratio and the same molecular weight, the conversion was affected by changing the type of initiator. For the reaction with KPS, low monomer conversion was obtained, about 48 %, while for the reaction when TBHP was used the monomer conversion achieved was 81%. In the reaction in which KPS initiator was used, it can be seen that at the beginning of the reaction (t=0), the monomer conversion is about 13% and in the reaction which TBHP initiator was used, the monomer conversion was lower at the same time. Regarding the average diameter of particles this parameter decreased when KPS initiator was used, and a narrow particle size distribution was observed. This might be due to the higher stability obtained at the surface of the particles due to the potassium persulfate groups from KPS located at the surface of the polymer particles which acted as stabilizers of the particles.

Table 11 shows the conditions and results of grafting efficiency for R3 and R12 reactions.

Table 11. Conditions and results of grafting efficiency and PMMA molecular weight on the surfactant free emulsion polymerization of MMA stabilized by PVAm.

Run	PVAm molecular weight (Da)	Initiator: PVAm (mol: mol)	GE (%)	PMMA molecular weight (Da)
R3	105 000	1:100	59	334545
R12	105 000	1:100	46	257810

The value of grafting efficiency for the R12 reaction was compared with the values of R3. These results can be seen in Figure 38.

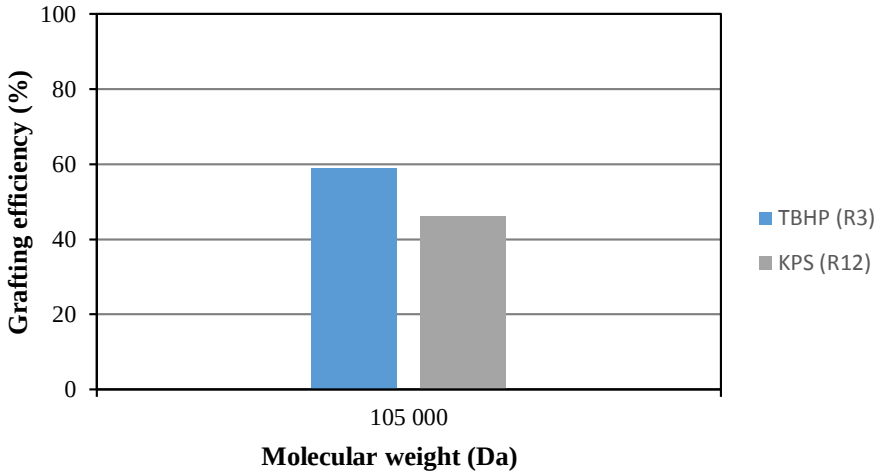

Figure 38. Representation of the grafting efficiency for reactions R3 and R12.

Analyzing the Figure 38 and the Table 10, it is possible to observe that the percentage of the grafting efficiency for R3 reaction was higher than the R12 reaction. The lower grafting efficiency obtained as well as the lower PMMA molecular weight measured when KPS was used might be due to the lower conversion obtained in this case.

4.3.6. Composition of PMMA/PVAm particles.

FT-IR technique was used to analyze the composition of the PMMA/PVAm particles. Because PVAm is not soluble in THF while PMMA homopolymer is soluble, the amphiphilic PVAm-g-PMMA copolymers and PMMA homopolymers were isolated by soxhlet extraction with THF. After extraction, the graft copolymers remained in the thimble filter while PMMA homopolymers were dissolved in THF.[7]

Figure 39 shows the FTIR spectra for the polyvinylamine, PVAm-g-PMMA and for isolated PMMA homopolymers.

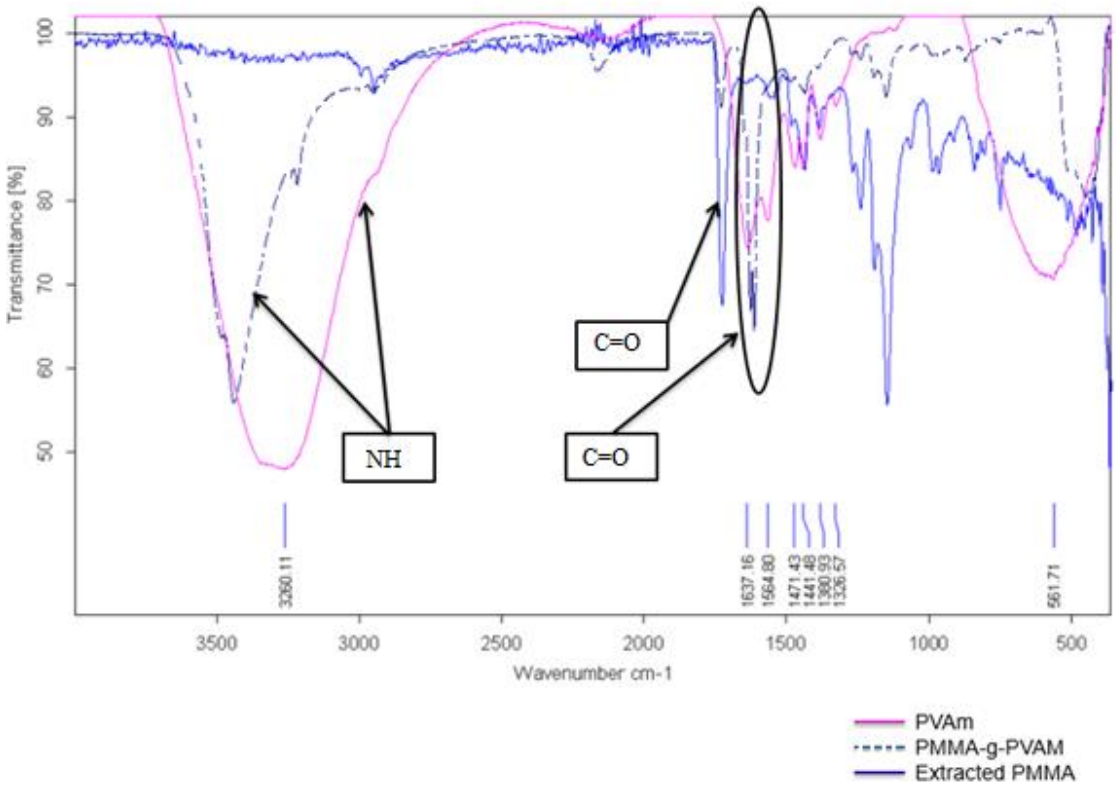

Figure 39. FT-IR spectra of PVAm, PMMA-g-PVAm and extracted PMMA.

Analyzing Figure 39, the spectrum of the polymer extracted from particles is exactly the same as compared with the standard IR spectrum of PMMA, confirming the formation of the PMMA homopolymer. The spectrum of PVAm-g-PMMA shows strong amine peaks around 3450 cm^{-1} and carbonyl peak at about 1700 cm^{-1}, which clearly indicates the formation of the graft copolymers.

4.4. References list

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Chapter 5

5.1. Conclusions

The PVAm, water soluble polymer, was synthesized through a two-step reaction: first the free radical polymerization in water using AIBA as initiator to generate PNVF and second hydrolysis of the preformed PNVF polymer to produced PVAm polymer under basic conditions.

During the free radical polymerization, it was concluded that was possible to obtain poly (N-vinylformamide) solutions with different molar masses by aqueous solution polymerization by conveniently varying temperature, initiator and monomer concentration.

The successful synthesis of PVAm through hydrolysis was confirmed by ^{1}H NMR spectra. The as-prepared PVAm was used for the synthesis of PMMA/PVAm particles. These particles were synthesized via surfactant free emulsion polymerization of MMA using PVAm was stabilizer induced by a small amount of TBHP in aqueous medium amphiphilic graft copolymers and PMMA homopolymers were generated concurrently to form highly monodispersed particles with diameters in the range of 90-760 nm. The formation of graft copolymers and homopolymers was confirmed by FT-IR. TEM micrographs revealed that the particle had a well-defined core-shell nanostructure and indicated that PMMA: PVAm particles displayed a rough morphology. The effects of reaction pH, molar ratio of TBHP: PVAm, molecular weight of PVAm and initiator type have been systematically investigated with respect to the monomer conversion, particle size and size distribution, grafting percentage and surface morphology. The monomer conversion increased with the increase of the pH reaction and with decreases of molar ratio TBHP: PVAm. This reaction achieved the optimum molar ratio where the monomer conversion was higher. The optimum molar ratio was changed with molecular weight of PVAm. Thus, it was possible to conclude that when molecular weight of PVAm decrease, the optimum molar ratio increase, however, for the experiments realized with lower molecular weight, it was not possible to distinguish the optimum molar ratio of TBHP: PVAm. When the molar ration of TBHP: PVAm decrease the particle size increase and the size distribution became wider. It was also found that the grafting efficiency of the PMMA increased with increase of the reaction pH and decrease of the molar ratio of the TBHP:PVAm. With the substitution of initiator TBHP for KPS in the reaction, it was

conclude that initiator KPS in contact with amino groups formed redox pairs and produced graft copolymers and PMMA homopolymers.

5.2. Limitations and Future works

During this labor others studies should be performed, but it was not possible to carry them in useful time. One of the things that should have been done, was the measurement of the molecular mass of PNVF-co-PVA after hydrolysis, so for further investigations it is proposed this measurement.

In a future investigation, for a more accurate conclusion, it will be necessary to carry out a further investigation to synthesize PolyNVF with other molecular weights. The surfactant free emulsion polymerization should be carried out with lower molar ratio of initiator:PVAm.

The new application areas of PMMA/PVAm particles should be investigated.

Appendix

Appendix I. Characterization methods

I.1. Characterization of initiator (AIBA)

AIBA was characterized by ^{1}H NMR and ^{13}C NMR spectrum. This characterization was made to make sure that the peaks of the polymer appeared in ^{1}H NMR and ^{13}C NMR were from the AIBA. The following figures, presents the ^{1}H NMR and ^{13}C NMR of the AIBA.

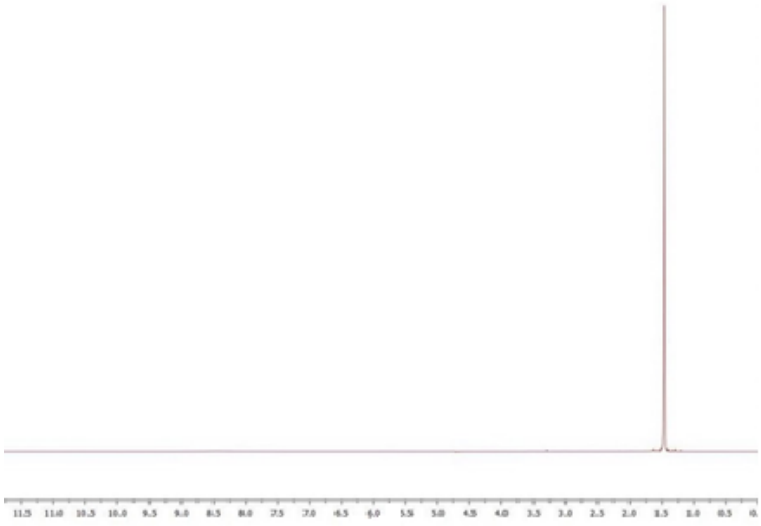

Figure I.1. Illustration of ^{1}H NMR spectrum (400 MHz, D_2O) of the initiator AIBA.

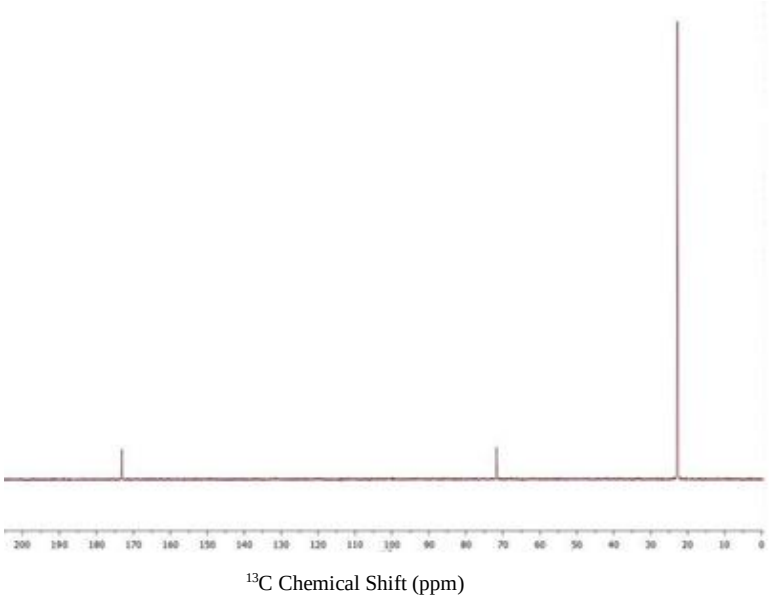

Figure I.2. Illustration of ^{13}C NMR spectrum (400 MHz, D_2O) of the initiator AIBA.

I.2. Molar mass of poly (N-vinylformamide)

The molar mass of poly (N-vinylformamide) was measured by AF4.The equipment was composed by a LC20 pump (Shimadzu) coupled to a DAWN Heleos multiangle (18 angles) light scattering laser photometer equipped with an He-Ne laser (λ=658 nm) and the Optilab Rex differential refractometer (λ=658 nm) (all from Wyatt Technology Corp.,USA).

The separation in AF4 equipment is achieved with no stationary phase, solely by a flow in an open channel where a perpendicular flow is applied. The channel consists of two plates joined together that are separated by a spacer. The bottom plate is permeable, made of porous frit covered by a semi permeable membrane with a cutoff of 10 KDa. The membrane is permeable for the molecules of carrier, but impermeable for the polymer molecules (Mw > 10 KDa) and therefore keeps the sample in the channel so that it is directed by flow to the channel outlet. AF4 flow control was maintained with a Wyatt Eclipse 3 AF4 Separation System Controller.

I.3. Spectra's of NMR for PVAm obtained through basic Hydrolysis.

The hydrolysis conversion was calculated through the ^{1}H NMR spectrum. The following figures, shows the ^{1}H NMR spectrum for PNVF1, PNVF3 and PNVF4 during the hydrolyze time.

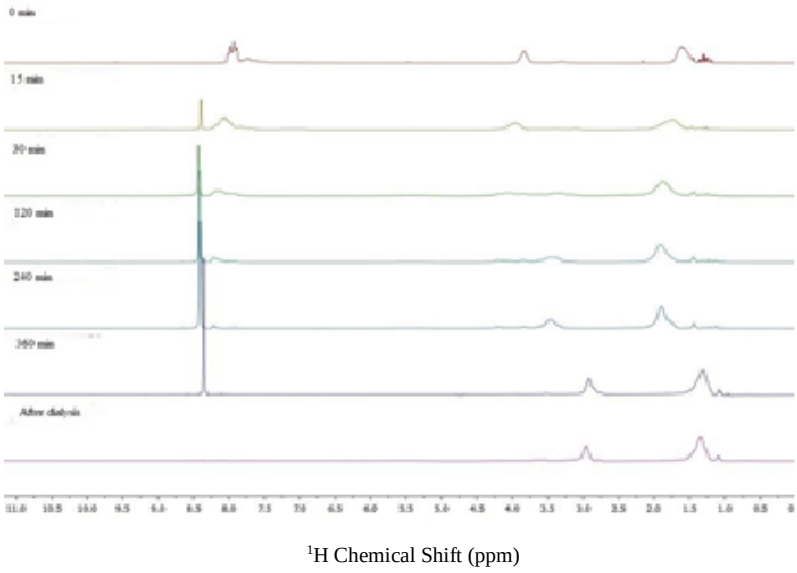

Figure I.3. ^{1}H NMR spectra of PNVF1 polymer at different reaction times (0, 15, 120, 240 and 360 min) and after dialysis

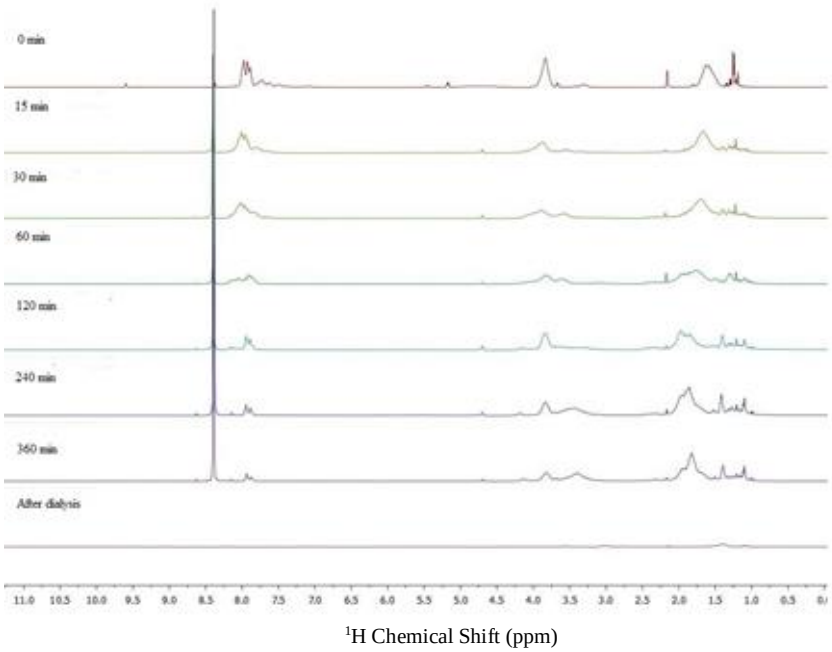

Figure I.4. [1]H NMR spectra of PNVF3 polymer at different reaction times (0, 15, 30, 60, 120, 240 and 360 min) and after dialysis

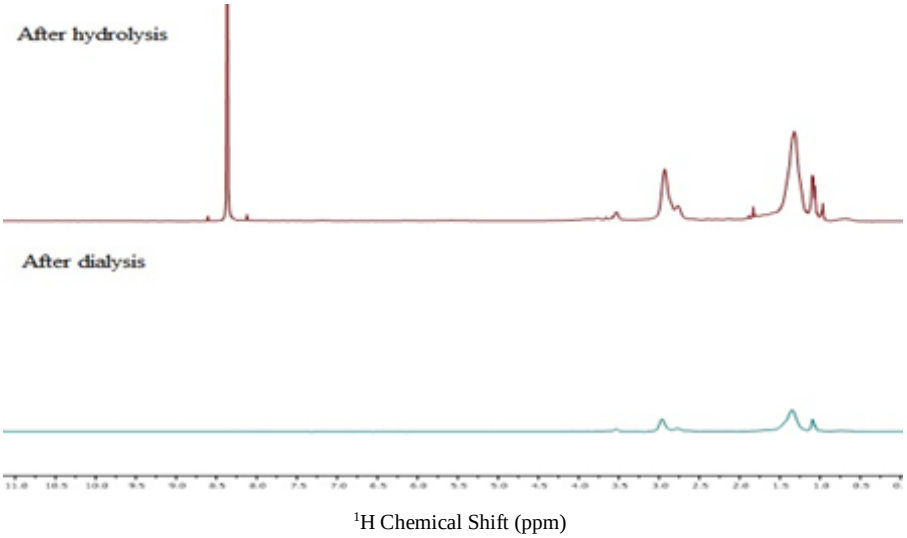

Figure I.5. [1]H NMR spectra of PNVF4 polymer at 0 min and after dialysis.

I.4. Calculation of the molar ratio of Initiator:PVAm.

The molar ratio was calculated with respect to PVAm weight. As an example, to calculate the molar ratio Initiator:PVAm= 1:50.

$$n_{initiator=\frac{n_{PVAm}}{50}} \quad (1)$$

I.5. Grafting efficiency

The grafting efficiency by definition is the fraction of polymer (PMMA) that is not soluble in a good common solvent such as tetrahydrofuran (THF). The grafting efficiency was measured by soxhlet extraction. To measure the grafting efficiency, Glass Fibre (19x99 mm Whatman) were used as filter. A few drops of PMMA/PVAm were placed on the filter and dried overnight at 60 ºC. The filter together with the dried polymer was weighed (weight of total polymerized MMA) and a continuous extraction with THF under reflux in the soxhlet for 24 h was done afterward. After this period of time, the wet filter was weighed and dried overnight. Finally, the weight of the dry sample was taken.

I.6. Particle size and size distribution of PMMA/PVAm particles

The particle size and the size distribution were measured by dynamic light scattering (Nanosizer Malvern).

Samples were prepared by diluting a fraction of the latex with distillated water. The analysis was carried out at 25 ºC and each rub consisted in 1 minute of temperature equilibration followed by 3 size measurements per sample.

I.7. PMMA molecular weight

The PMMA molecular weight was measured through the SEC/GPC. The set up consists of a pump (Waters 2410) and three columns in series (Styragel HR2, HR4 and HR6, with pore sizes ranging from 102 to 106 Å). Chromatograms were obtained at 35 ºC using a THF flow rate of 1ml/min. The equipment was calibrated using polystyrene standards (5th order universal calibration) and therefore the molecular weight was referred to PS (no Mark-Houwink constants).

Appendix II. Some Results

II.1. Molar mass of poly (N-vinylformamide)

The molar mass of PNVF was analyzed by AF4, the following figure presents the graphs obtained for PNVF3 and PNVF4 polymers by this equipment that allows the calculation of the Mw, Mn and PDI. For the graphics we can see that there is two peaks for each samples, both in refractive index as light scattering. The molar mass was calculated by the average of the two peaks.

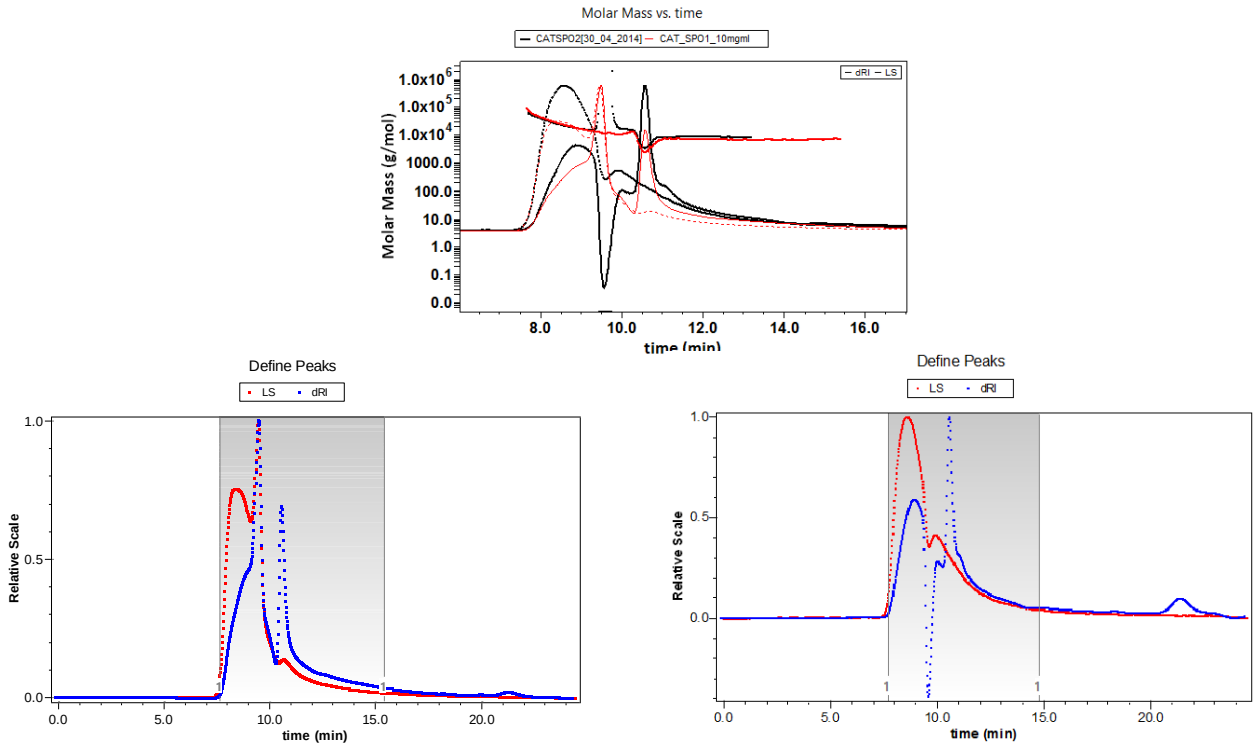

Figure II.1. Representation of molar mass of PNVF3 and PNVF4 polymer with time

II. 2. Molecular weight of PMMA

The molecular weight of PMMA homopolymers was analyzed by SEC/GPC. The following figures presents the distributions of molecular weight for PMMA homopolymers.

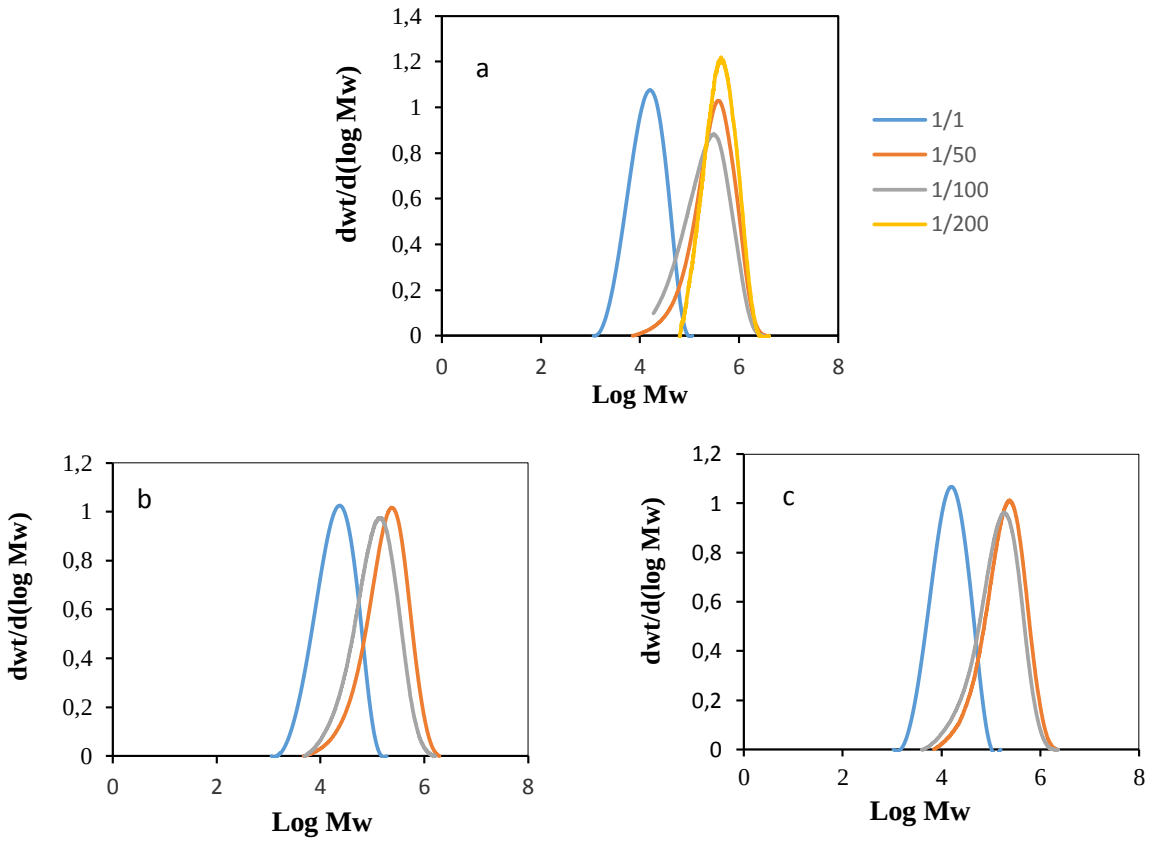

Figure II.2. Molecular weight distributions of PMMA homopolymers, obtained with different polymers: a) PNVF1; b) PNVF2 and c) PNVF4.

II.3. Experiments of DLS

During this work, was tested the variation of the particle size with the temperature and the concentration of the sample in dynamic light scattering (DLS). The figure II.3, shows this variation and can been seen that the temperature does not affect the particle size.

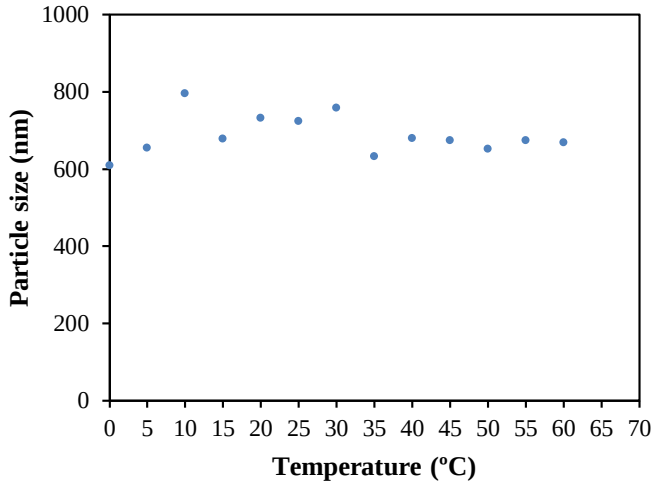

Figure II.3. Representation of particle size of the final latex (R3), varying the temperature of the DLS.

The figure II.4, presents the distribution of particle size, measured through the DLS, which in samples had different concentration. a) Represent the sample that was diluted in water and b) represent the sample without dilution (only latex).

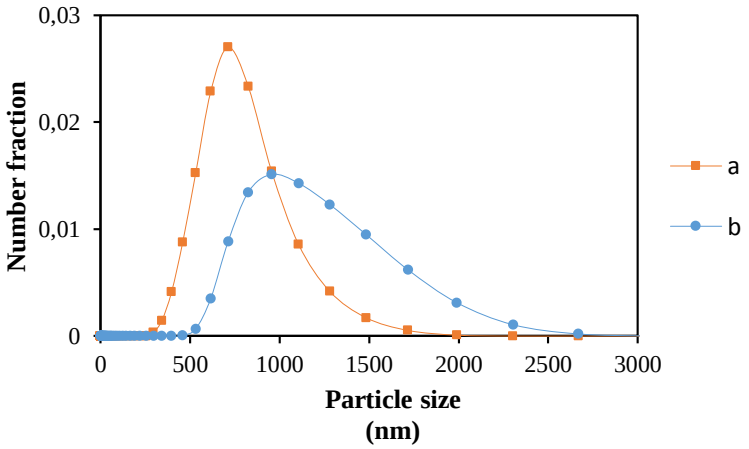

Figure II.4. Comparison of particle size distribution which in the sample a) was diluted in waster and b) was not diluted.

Analyzing the figure above, can been seem that the concentration of samples influenced the particle size.