RZESZOW UNIVERSITY OF TECHNOLOGY
FACULTY OF CHEMISTRY
Department of physical chemistry

MASTER'S DIPLOMA THESIS

STUDY OF REVERSIBLE - DEACTIVATION RADICAL POLYMERIZATION

Eng. Ramón Peña

Work supervisor: Paweł Chmielarz, DSc, PhD, Eng., Associate Prof.

Rzeszów, 2020

I would like to thank the Promoter Professor Paweł Chmielarz, for having patience and helping me in the key points of this work.

To Karolina Surmacz without whom this work would have been impossible to carry out, I am very grateful.

And in general, to the Rzeszow University of Technology for having welcomed and treated me with great respect and always attending to my needs.

Index

1. ABSTRACT

1.1. ENGLISH ABSTRACT

The headline aim of the research is the optimization of the synthesis of poly(D-limonene) homopolymers in miniemulsion system. Reactions were conducted using Atom Transfer Radical Polymerization (ATRP) technique, controlled by electrical current (*e*ATRP). This technique allows for simultaneous growth of all chains affording good control over the physicochemical properties of polymers. In this work, the kinetic was also analyzed and the rate constants of polymerization reactions based on gravimetric and GPC analysis were determined.

1.2. SPANISH ABSTRACT

El objetivo principal de la investigación es la optimización de la síntesis de homopolímero de poli (D-limoneno) en el sistema de miniemulsión. Las reacciones se llevarán a cabo utilizando la técnica de Polimerización Radical por Transferencia Atómica (ATRP), controlada por corriente eléctrica (*e*ATRP). Esta técnica permite el crecimiento simultáneo de todas las cadenas, proporcionando un buen control sobre las propiedades fisicoquímicas de los polímeros. En este trabajo, también se analizará la cinética y se determinará velocidad constante de las reacciones de polimerización basadas en análisis gravimétricos y GPC.

1.3. POLISH ABSTRACT

Głównym celem badań jest optymalizacja syntezy homopolimerów poli(D-limonenu) w układzie miniemulsji. Reakcje prowadzono za pomocą polimeryzacji rodnikowej z przeniesieniem atomu (ATRP), w której aktywatory regenerowane są w skutek przepływającego ładunku elektrycznego (*e*ATRP). Metoda ta pozwala na jednoczesny wzrost wszystkich łańcuchów przy zachowaniu dobrej kontroli nad właściwościami fizykochemicznymi łańcuchów polimerowych. W pracy przeanalizowana została również kinetyka i wyznaczone zostały stałe szybkości reakcji polimeryzacji na podstawie analizy grawimetrycznej i GPC.

LIST OF ABBREVIATIONS APPLIED

ATRP	- Atom transfer radical polymerizacion
ICAR	- Initiators for continuous activator regeneration
AGET	- Activators generated by electron transfer
SARA	- Supplemental activator and reducing agent
***e*ATRP**	- Electrochemically mediated atom transfer radical polymerization
SDS	- Sodium dodecyl sulfate
EBiB	- Ethyl α-bromoisobutyrate
HD	- Hexadecane
RDRP	- Reversible deactivation radical polymerization
TPMA	- Tris(2-pyridylmethyl) amine
MW	- Molecular weight
MWD	- Molecular weight distributions
WE	- Working electrode
RE	- Reference electrode
CE	- Counter electrode
***se*ATRP**	- Simplified electrochemically mediated atom transfer radical polymerization
CV	- Cyclic voltammetry

2. PURPOSE AND SCOPE OF WORK

The objective of the work is the use of simplified electromechanically-mediated atom transfer polymerization (*se*ATRP) in miniemulsion media for the preparation of poly(D-limonene), including:

- Review of the literature related to ATRP methods and especially to the preparative electrolysis.
- A description of the *se*ATRP technique, considering the mechanism, advantages, and disadvantages of this approach.
- Characteristics of the polymerization process using the *se*ATRP technique.
- Analysis of the mechanism, kinetics study and determination of the rate constants of polymerization reactions.

3. INTRODUCTION

In this thesis simplified electronically mediated atom transfers radical polymerization (*se*ATRP) was studied. Preparative electrolysis allows for the fully control preparation of well-defined polymers with low dispersity, predictable molecular weight of prepared macromolecules and retained chain-end functionality.

In recent years, ATRP techniques were rapidly developed to remove the accompanying limitations and make these solutions more clear and industry-relevant approaches. Numerous modifications of the ATRP technique have been developed.

Currently, it is not only considered that the reactions are effective, but it must be ecological and environmentally friendly. Therefore, many synthesis studies are carried out in water for polymerization of hydrophilic monomers or in miniemulsion media for polymerization of monomers with hydrophobic characteristics.

In the case of miniemulsion, organic solvents are removed to replace them with aqueous media. Implementing the processes that occur in miniemulsion with the ARTP technique, it is possible to obtain products with very complex structures that also maintain safe conditions for the environment.

The miniemulsion consists of mixing two phases in a liquid state that are insoluble. In this way, two separate phases are achieved that can be stabilised using surfactants or co-surfactants.

This work analyses the use of *se*ATRP techniques for the preparation of precisely defined polymers, an examination of the mechanism, and indicating the advantages of this method compared to other methods. Additionally, among the use of external control as an eco-friendly aspect, removing an additional chemical reducing agent from reaction mixture, the miniemulsion media was used for further development of more environmental aspects of ATRP synthesis. The polymerization process was described in detail, considering the kinetics investigation by determination of the rate constants of ATRP synthesis. Moreover, the miniemulsion ATRP was examined, considering the interfacial catalysis and ion-pair catalysis – the principles of miniemulsion polymerization.

Firstly, the steps to prepare miniemulsion will be described. The next step will be a detailed description of the electrochemical cell and what reactions take place at each electrode.

Finally, analysis of the data obtained will be presented, indicating the accuracy in the choice of ATRP technique in the preparation of poly(D-limonene).

4. THEORETICAL DESCRIPTION

In the theoretical description about the analysis of the principles of ATRP approach will be showed, giving a complete overview of the application of ATRP methods in the preparation of precisely defined polymer materials.

4.1. ATRP MECHANISM

Among traditional radical polymerization, these type of techniques allows to obtain polymeric structures in a well-controlled manner.

The ATRP mechanism is based on a continuous regeneration process of transition metal in its reduced form. The reduced form of the catalytic complex activates alkyl halide, initiating polymerization, and thus the radicals are generated. It results in the propagation process, and monomers are incorporated into polymer chains in a control manner, forming well-defined structures with predetermined molecular weights.

However, a normal ATRP had a high catalyst loading (10,000 ppm), it was undesired due to the sensitivity of the catalyst for the action of air and oxidants, and required additional stages of purification to complete elimination of the transition metal complex from the final product. To solve this problem, a new solution was created by and additional redox cycle, provided by reducing agents that continuously regenerate the catalytic complex to form an activator.

The regeneration of activator (Cu^{I}) is possible with the use of chemical agents or external stimuli. There are [1]:

1. METHODS WITH CHEMICAL REDUCING AGENTS:
    a. (ICAR) ATRP → Radical initiators in continuous regeneration of activators.
    b. (ARGET) ATRP → Activator regenerated by electron transfer.
    c. (SARA) ATRP → 0-value metals in supplemental activators and reducing agents.
2. EXTERNALLY CONTROLLED METHODS:
    a. (*e*ATRP) → Electrochemically mediated.
    b. (foto-ATRP) → Photochemically mediated.
    c. (mechano-ATRP) → Mechanically induced.
    d. (sono-ATRP) → Ultrasound mediated.

The last considerations revolve around applying techniques with external factors to keep control over process. These methods allow to avoid the use of additional reduction agents and thus eliminate unwanted by-products. Also, it enables the temporal control over the polymerization by

switching on/off the external stimuli. Temporal control provided the examination for the living character of the polymerization and the polymeric materials with predictable molecular weights.

This type of technique has a few advantages:

1. polymerization rate is controlled by external stimuli without an additional chemical compound, thus removing stages of purification and the synthesis if eco-friendly,
2. easy to use and apply,
3. it is versatile since it can polymerize both hydrophobic and hydrophilic monomers.

Based on these concepts, the mathematical model that will predict the reaction speed will be analysed. It starts from the basis of ATRP and the polymerization reaction.

Figure 1: ATRP method polymerization path [2].

The ending part also contains an equilibrium constant that defines that process, and which will be necessary to predict the mathematical model. Therefore, we start from the following elements:

- K_{act}: Activation constant.
- K_{deact}: Deactivation constant.
- K_P: Propagation constant.
- K_T: Termination constant.
- X: Halogen.
- L: Ligand
- R_n-X: Alkyl halide.
- R_p: Reaction rate.

With this data, the reaction rate equation is constructed as follows [3][4]:

$$R_p = K_P \cdot [M] \cdot [R_n{}^*]$$

$$K_{ATRP} = \frac{K_{act}}{K_{desact}}$$

The separate reactions are as follows:

Activation → $\frac{d[R_n^*]}{dt} = K_{act} \cdot [R_n^* X] \cdot [Cu^I L]$

Deactivation → $-\frac{d[R_n^*]}{dt} = K_{desact} \cdot [XCu^{II} L] \cdot [R_n^*]$

$$K_{act} \cdot [R_n^* X] \cdot [Cu^I L] = -K_{desact} \cdot [XCu^{II} L] \cdot [R_n^*]$$

$$[R_n^*] = -\frac{K_{act} \cdot [R_n^* X] \cdot [Cu^I L]}{K_{desact} \cdot [XCu^{II} L]}$$

If we substitute in the reaction rate equation:

$$R_p = K_P \cdot [M] \cdot \frac{K_{act} \cdot [R_n^* X] \cdot [Cu^I L]}{K_{deact} \cdot [XCu^{II} L]}$$

$$R_p = K_P \cdot [M] \cdot K_{ATRP} \cdot \frac{[R_n^* X] \cdot [Cu^I L]}{[XCu^{II} L]}$$

Keep in mind that K_{ATRP} is affected by the temperature and pressure of the system.

4.2. ULTRASONICATION-INDUCED ATRP

The analysis of the ultrasound method will allow a better understanding of what are externally controlled methods, and thus better explain the events that occur in the reaction to be studied.

The acoustic cavitation effect (mechanical effect) in a fluid medium causes the formation and implosive collapse of bubbles in a liquid. This produces increase in temperature and pressure conditions.

The effect through by ultrasound can be divided in two:

I. physical sonochemistry: Related to the physical effects of bubble collapse. This produces reactive radical species.
II. mechanical chemistry: Arises from the strong cutting gradients produced by the collapse of the bubble. Created forces can break covalent bonds and this can create an electrical charge in response to a change of pressure in piezoelectrical materials.

In ATRP we can use both approaches:

Mechanically induced ATRP (mechano-ATRP) → Mechanical driving force that is sufficient to induce an electric charge in response to applied mechanical stress with the use of piezoelectric [6].

Ultrasound-mediated ATRP (sono-ATRP) → The driving force for regeneration of an activator are hydroxyl radicals in aqueous medium and additional radical species reactive from solvent / ligand / reagent in an organic solvent [7].

To take sonification into account, it must be known that the applied force is focused on the transfer of electrons. It is achieved by transducing a mechanical stimulus into an electrical signal. To obtain this, piezoelectric nanoparticles are used (the piezoelectric effect, which induces an electric charge in response to mechanical stress applied with ultrasound).

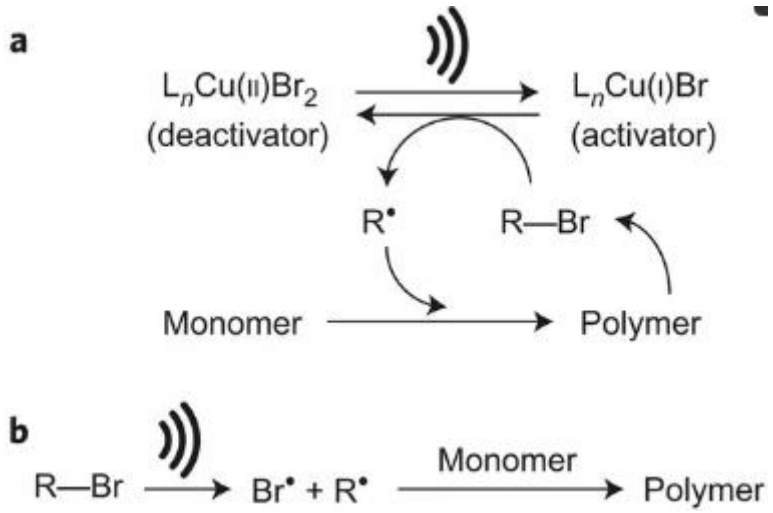

Figure 2: Two of potential routes for the initiation of polymerization process by ultrasound agitation [8].

a. Reduction of the deactivator by the piezocatalytic effect that results in the formation of an activator followed by the generation of radicals and growth of the polymer chain.
b. Ultrasound-mediated radical generation, directly initiating radical polymerization.

Considering the ATRP methods studied until now, one of the most interesting is sono-ATRP that can be used in homogeneous and dispersed media. In this case, we can use water as a solvent in sono-ATRP for both hydrophilic and hydrophobic monomers polymerization. Thanks to that the use of piezoelectric materials is not necessary.

Compared to the piezocatalytic approach, the application with ultrasonic force was characterized by a different mechanism instead of a mechanically induced solution, and thus avoids the use of additional reducing chemical agents. As the wave propagates through the aqueous medium, the hydroxyl $HO^{\bullet}$ activator is produced, this is due to acoustic cavitation.

The formed radicals are precursors to forming carbon radicals by reacting with vinyl monomers and initiating polymerization by direct reduction of Cu^{II}. To maintain control over aqueous ATRP, it is important to use a halide salt. This is because the dissociation of bromide anions in deactivating species is reduced. And so, its concentration is increased by reducing hydrolysis of a brominated form of an initiator or growing polymer chain [9].

In the case of aqueous dispersed sono-ATRP, additionally should be used surfactant should be additionally used, in order to acts as an anionic surfactant, results in the formation of neutral ion pairs that have the ability to activate the polymer within the hydrophobic monomer droplets reflecting interfacial catalysis.

In summary, the mechanism would be the following:

In the case of sono-ATRP it will be investigated in miniemulsion, in this way it is possible to synthesize homopolymers and copolymers with hydrophobic characteristics in aqueous media with the use of a strongly hydrophilic complex. Catalysis is described by two mechanisms: interfacial and ion-pair catalysis. When ultrasonication occurs, the catalytic complex is reduced on the surface of the monomer droplets – interfacial catalysis

Polymerization starts with interfacial catalysis, then combined with sodium dodecyl sulfate (SDS), which acts as an anionic surfactant, and results in the formation of neutral ion pairs, which have the ability to activate the polymer within hydrophobic micelles, this is how the ion-pair catalysis is reflected. The residual part of the catalytic complex remains in the aqueous phase [10].

4.3. ELECTROCHEMICALLY ATRP

As it is known, reversible deactivation radical polymerization (RDRP) allows for the preparations of polymers with a precisely defined molecular weight in terms of their structure or functionality. Among all the RDRP techniques, ATRP stands out, which is the one being used in this thesis, since it is compatible with many functional monomers and tolerates the influence of variable reaction conditions. This allows for the synthesis of block homopolymers and copolymers with well-defined and complex structures.

Atom transfer radical polymerization (ATRP) is a process based on reactions with various transition metals such as copper, iron, and nickel. Although the most frequent is the copper complex with an appropriate ligand, which catalyses the activation of an alkyl halide and this generates a radical.

Quickly, when one or more monomers join, the macroradical is deactivated again under the influence of the transition metal complex, forming a higher oxidation state. If the ATRP reaction is well controlled the equilibrium shifts strongly towards the inactive alkyl halide, which is due to the

presence of the X-Cu^{II} / L complex and allows to obtain products with a narrow molecular weight distribution [11].

The ATRP method is still improving by applying complex catalysts with higher activity and regeneration and employing a variety of techniques of electron transfer to give better control of the polymerization processes. One of the best example of this is the electrochemically-mediated atom transfer radical polymerization (*e*ATRP) technique.

This technique starts with the application of an appropriate electric potential or current. This results in the reduction of the X-Cu^{II}/L catalytic complex to its active form with a lower oxidation state of X-Cu^{I}/L, on the surface of the working electrode. The resulting reduced form of the complex reacts with an alkyl halide, which acts as an initiator. This generates radicals that bind the monomer by propagation, and subsequently they are deactivated again while taking an inactive form [12]. Regulation of the rate of polymerization reaction results in the ability to control the structure of the synthesized compound and is achieved by controlling the concentration ratio of activator to activator by selecting the appropriate electrochemical potential/current.

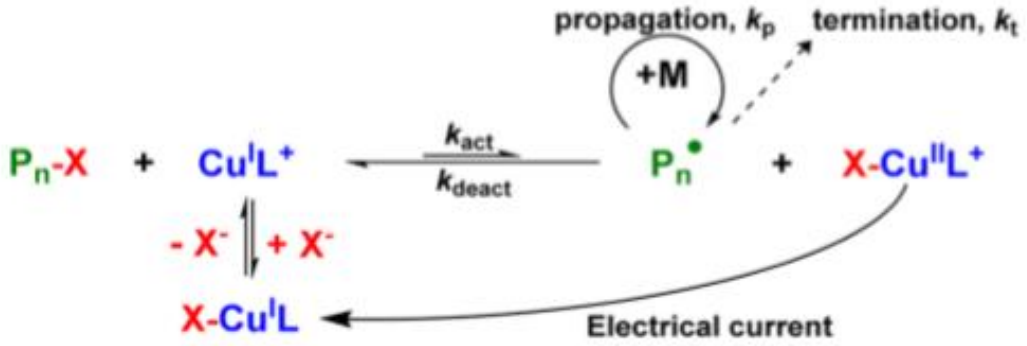

Figure 3: Mechanism of eATRP [8].

The application of *e*ATRP allows reactions to be carried out using a very active copper catalyst, at low concentration – on ppm level. This allows the technique to be much better in industrial applications due to the environmentally friendly approach. When initiating reactions using the appropriate electrochemical potential, it is not necessary to use chemical compounds as reducing agents. This method is characterized by reusing the catalyst. By using much negative potential than cathodic potential, the metal is deposited on the surface of the working electrode. Changing the potential to positive allows the catalyst to be released from the electrode to the solution.

Potential variations allow the reaction to be stopped and resumed at any time, allowing a greater level of control over the reaction course and the synthesis of products. But this method also has some limitations that are mainly related to the reaction system in which the polymerization is carried out [13].

The most common is the one that uses three electrodes: working (WE), reference (RE), and counter electrode (CE). This solution requires the separation of both the reference and counter electrode from the working electrode. If an undivided cell is used, placing CE directly into reaction mixture could occur the oxidation of the transition metal complex at a lower degree of oxidation (activator) to the form of a catalytic complex at a higher degree of oxidation (deactivator), which is highly undesirable. The other undesired opportunity is the oxidation of halide ions present in the reaction mixture. Also, there could not be excluded the oxidation of the solvent or supporting electrolyte [13].

However, these disadvantages do not make the technique useless. The complexity of the *e*ATRP reaction setup can be minimised by using a sacrificial anode (CE). This procedure, referred to as simplified *e*ATRP (*se*ATRP), does not require the separation of CE from reaction mixture so it can be directly inserted into the reaction mixture. Additionally, usage of water as a solvent makes the process gentler on the environment and therefore more eco-friendly and eliminates the need for potentially dangerous and volatile organic solvents. This makes the combination of the ATRP method and the miniemulsion polymerization find application in the industry, for example, biotechnology, to produce polyelectrolytes, as drug carriers.

4.4. MECHANISM IN MINIEMULSION MEDIA

A miniemulsion polymerization process is a technique that allows obtaining versatile species of polymers and structural materials. Miniemulsion consists of small, stable, closely spaced droplets in a continuous phase. This system can be obtained with mixing using ultrasound. High stability off such a system is guaranteed by adding an amphiphilic component, as a surfactant, and an auxiliary stabilizer, soluble, and evenly distributed in the drop phase. These droplets act as nanoreactors.

The basis for obtaining a miniemulsion is the use of a combination of monomer, surfactant, and co-surfactant in an aqueous environment, the system is subsequently subjected to shear forces. The use of the shear breaks up the largest monomer droplets into small ones that also correspond to the range of polymer particle sizes obtained with this technique.

The sizes of the monomer droplets and the polymer particles can be regulated by modifying the amount of surfactant, the added co-surfactant, and the selection of appropriate shear forces [14].

The surfactant is used to prevent the merging of the monomer droplets due to the action of the chaotic movement caused by collisions with fluid particles. And in turn, the co-surfactant

protects the penetration of monomer from small into large drop particles (called as Ostwald ripening).

In these assemblies there are no micelles, so the nucleation of the particles is produced by the entry of radicals in the drops. Initiators used in the miniemulsion polymerization can be water soluble or monomer soluble.

In the case of the *e*ATRP technique [14], a system of two catalysts can be used: hydrophobic and hydrophilic. The working electrode remains in contact with the aqueous phase; therefore, the role of the water-soluble catalyst is to transfer the electrochemical pulse to a hydrophobic catalyst enclosed in dispersed monomer droplets [15]. It has also been observed that it may be sufficient to use only a hydrophilic catalyst if its combination with anionic surfactant is used. The system that connects the catalyst to the surfactant generates ion pairs that transport the catalyst to the hydrophobic monomer droplets. The generated ion pairs can be within or on the surface of the monomer droplets. Most of them bind to the monomer-water interface, resulting in an interfacial catalysis, which enables the expected polymer to be successfully obtained, allowing for controlled polymerization [16].

The combination of miniemulsion polymerization and ATRP technique has resulted in interesting industrial applications, for example, in the preparation of controlled released substances for medicines or the encapsulation of dyes and cosmetics. In this way, a very interesting means of polymerization is achieved.

In the experimental part will be studied *se*ATRP method, adapted to more precise and heterogeneous miniemulsion media. As explained, thus it is possible to take advantage of the concept of ion-pair and interfacial catalysis, it is also possible to promote a unique catalyst mechanism in the presence of anionic surfactant (SDS). This will be the type of polymerization that we are going to analyse the most to demonstrate that it can be considered as a very interesting and promising possibility in the field of ATRP.

5. EXPERIMENTAL RESULTS

In this section we will explain how the experiments have been carried out to predict the behaviour of the reactions and thereby reach conclusions that say whether the process is correct or not.

5.1. REAGENTS

Table 1: Phase distribution.

Organic phase	**Aqueous phase**
Ethyl α-bromoisobutyrate (EBiB) – initiator	*Water - dispersing medium*
n-hexadecane (HD) - cosurfactant	*SDS - surfactant*
Limonene - monomer	*NaBr – halide salt*
	$Cu^{II}Br_2$/TPMA – catalytic complex

Of these compounds, the following can be highlighted for their importance:

- Initiator: Ethyl α-bromoisobutyrate (EBiB)

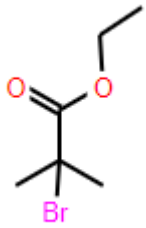

Figure 4: Initiator Initiator- Ethyl α-bromoisobutyrate (EBiB)

Molecular mass: 229.9 $^{g}/_{mol}$

Boiling point: 162 ºC

Relative density: 1.86 $^{g}/_{cm^3}$ in 20ºC

- Cosurfactant: n-hexadecane (HD)

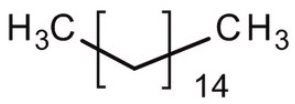

Figure 5: Cosurfactant - n-hexadecane (HD)

Molecular mass: 226.448 $^{g}/_{mol}$

Boiling point: 287 ºC

Relative density: 0.77 $^{g}/_{cm^3}$ in 20ºC

- Monomer: Limonene

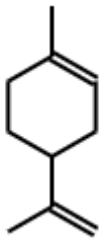

Figure 6: Monomer - D-limonene

Molecular mass: 136.23 $^{g}/_{mol}$

Boiling point: 176 ºC

Relative density: 0.8411 $^{g}/_{cm^3}$ in 20ºC

- Surfactant: Sodium dodecyl sulfate (SDS)

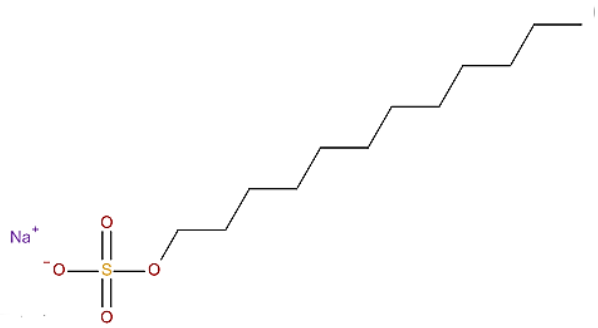

Figure 7: Surfactant - sodium dodecyl sulfate (SDS)

Molecular mass: 288.372 $^{g}/_{mol}$

Boiling point: 206 ºC

Relative density: 1.01 $^{g}/_{cm^3}$ in 20ºC

- Catalytic complex: Copper(II) bromide

Br-Cu-Br

Figure 8: Catalytic complex – copper (II) bromide

This component is used as a catalytic complex that binds to the ligand in the solution to be added to the mixture. Its properties are as follows:

Molecular mass: 223.35 $^{g}/_{mol}$

Boiling point: 1393 ºC

Relative density: 4.71 $^{g}/_{cm^3}$ in 20ºC

- Ligand: Tris(2-pyridylmethyl) amine (TPMA)

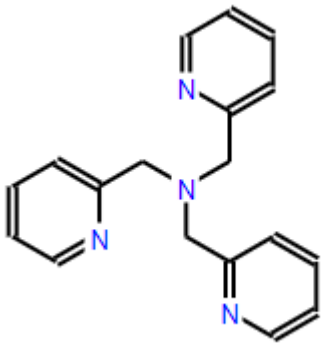

Figure 9: Ligand - Tris(2-pyridylmethyl)amine (TPMA)

Molecular mass: 290.4 $^{g}/_{mol}$

Boiling point: 409.8 °C

Relative density: 1.2 $^{g}/_{cm^3}$ in 20°C

5.1.1. Preparation of reaction mixtures

- Reaction 1

Two phases have been prepared:

Organic phase: a stock solution of Limonene (monomer), EBiB (initiator) and HD (co-surfactant) was prepared.

Aqueous phase: the solution of catalyst complex (0.05 M $Cu^{II}Br_2$/TPMA solution in distilled water), NaBr (supporting electrolyte), and SDS (surfactant) were dissolved in appropriate volume of distilled water.

Table 2: Composition of the organic phase in reaction 1.

Reaction 1		ratio	n (mmol)	conc (M)	m (g)	V (mL)
org. phase	LIM	200.00	17.40	1.09	2.37	2.82
	EBiB	1.00	0.09	0.01	0.02	0.01
	HD	13.02	1.13	0.07	0.26	0.33

Table 3: Composition of the aqueous phase in reaction 1.

Reaction 1		ratio	n (mmol)	conc (M)	m (g)	V (mL)
aq. phase	SDS	5.90	0.51	0.03	0.15	
	NaBr	15.42	1.34	0.08	0.14	
	$CuBr_2$/L	0.10	0.01	0.05	0.00	0.17
	Water	8079.25	702.84	43.93	12.67	12.67

Reaction 2

Table 4: Composition of the organic phase in reaction 2.

Reaction 2		ratio	n (mmol)	conc (M)	m (g)	V (mL)
org. phase	LIM	200.00	136.23	1.09	3.56	4.23
	EBiB	1.00	195.05	0.01	0.03	0.02
	HD	13.01	226.45	0.07	0.39	0.50

Table 5: Composition of the aqueous phase in reaction 2.

Reaction 2		ratio	n (mmol)	conc (M)	m (g)	V (mL)
aq. phase	SDS	5.86	288.37	0.03	0.22	
	NaBr	15.24	102.89	0.08	0.21	
	$CuBr_2$/L	0.20	0.03	0.05	0.01	0.52
	Water	7950.33	18.02	43.30	18.73	18.73

The organic and aqueous solutions were mixed and ultrasonicated for 20 minutes in the ultrasonic bath.

5.1.3. Complete dissolution

Table 6: Fundamental values of dissolution.

	Temp (ºC)	Applied potential (mV)	Time (h)	Conc. of cat. complex (ppm)
Reaction 1	65	-300	21	500
Reaction 2	65	-400	39.83	1000

To know the potential values that must be applied in each of the reactions, it is necessary to apply the following expression:

$$1) \quad E_{app} = E_{pc} - 100 \text{ mV}$$

$$2) \quad E_{app} = E_{pc} - 200 \text{ mV}$$

The applied potential was reduced in refer to cathodic potential of catalyst. In DMF solution, according to previous CV analysis E_{pc} in miniemulsion was established as E_{pc} = -200 mV.

The solution was bubbled with argon in electrochemical cell and the Pt mesh (WE), Al wire (CE), and SCE RE were prepared and located in this flask. After 20 min under Ar purge, the reaction was started with appropriate electrochemical potential. The reaction was conducted in appropriate time. Samples were withdrawn periodically to follow the monomer conversion by gravimetric analysis, M_n (molecular weight) and $Đ$ (molecular weight distribution) were determined by GPC.

5.2. EQUIPMENT AND APPLIANCES

To carry out the experiment and to make the montage complete, the following materials were used:

- ✓ Magnetic stirrer Heidolph MR Hei-mixL.
- ✓ Thermostat Labo-Play ESM-3711-H.
- ✓ Analytical balances OHAUS SERIA PA, RADWAG WTB 200.
- ✓ Basic laboratory equipment (dishes, beakers, measuring cylinders, vials etc.)
- ✓ 3 electrodes: working, reference and counter electrode
    - Working electrode: Platinum electrode
    - Reference electrode: Saturated calomel electrode (SCE)
    - Counter electrode: Aluminium electrode
- ✓ Electrochemical cell.
- ✓ GPC: Polymer Standards Services [PSS] columns [guard, 10,5 10,3 and 102 Å]
- ✓ Potentiostat Autolab from Metroleum (AUT84337)

5.3. SYNTHESIS METHODOLOGY AND INVESTIGATION OF REACTION PRODUCTS

Next, we will analyse the steps that have been followed to obtain the results, and a detailed analysis of these.

5.3.1. Preparation of miniemulsion.

To prepare the miniemulsion the following steps have been taken:

1. First, we prepare the aquatic phase.

We clean the beaker with pressurized air so that we eliminate any possible water residue that may have remained. Then were weighed the SDS and NaBr in the amounts that have been previously calculated, for this the vessel is tared with the beaker.

And finally, the volumes of water and catalyst are added with a syringe.

Figure 10: Preparation of the aquatic phase.

1. Preparation of the organic phase.

First, the scale is weighed in the starter, and in the same container we add the necessary monomer mass that we have previously calculated. To add HD (cosurfactant) to the solution, it must first change phase since it is in a solid state, it is simply necessary to put it on the tap with hot water and it already changes phase. Finally, it added.

Figure 11: Preparation of organic phase

2. Mixing

To mix the two phases, first was added them to the same container, then add the solution to an ultrasound machine, thus consolidating the sample, causing the drops to separate from the organic phase, creating a homogeneous environment.

Figure 12: Mixing of phases

For the reaction to take place it is necessary to do it in an inert atmosphere, this is achieved by flowing a stream of argon over the cell so that the argon occupies the entire atmosphere of the reactor.

The organic and aqueous solutions were mixed and bubbled with argon in an electrochemical cell and the Pt (WE) disk, Al wire (CE) and SCE RE were prepared and placed in this flask. After 20 minutes under Ar purge, CV (cyclic voltammetry) was performed and the reaction started with an appropriate electrochemical potential (E_{app}). The reaction was carried out at the appropriate time. Samples were periodically withdrawn to follow monomer conversion by

gravimetric analysis, M_n (molecular weight) and $Đ$ (molecular weight distribution) were determined by GPC.)

5.3.2. Equipment assembly.

Figure 13: Platinum electrode

The platinum electrode is where Cu^{II} reduction occurs, therefore it plays the role of the anode. The following reaction occurs in it:

$$\textit{Reduction reaction: } Cu^{II} + e^{-} \rightarrow Cu^{I}$$

The nature of the working electrode can influence the course of electrochemical reactions, resulting in the formation of different products of constitution depending on the material of this compound. In this case it is a mesh electrode. While in the aluminium electrode the reverse reaction occurs. This electrode being the cathode.

Figure 14: Aluminium electrode

$$\textit{Oxidation reaction: } Al^{0} + 2e^{-} \rightarrow Al^{III}$$

The reference electrode (saturated calomel electrode (SCE)) is an electrode that has a known and stable equilibrium potential. It is used to measure the potential against other electrodes in an electrochemical cell. The liquid binding potential in these electrodes is minimized using high concentrations of potassium chloride as a filling solution, because the diffusion rates of these ions are very similar.

Figure 15: Reference electrode

The electrodes should not touch each other and not touch the walls. Furthermore, the electrodes must be immersed in the solution at equal heights, putting the working electrode in the centre and being the last to connect and the first to disconnect.

Figure 16: Assembly of the reactor where the reaction occurs.

Finally, the *se*ATRP reactor is as follows. All reaction system is heated in thermostat to 65ºC. It must be borne in mind that mixture must have an atmosphere of argon, which being an inert gas will not harm the reaction process.

5.3.2. Preparation of samples for GPC analysis

The GPC needs an explanation because it is a more precise and complicated measurement equipment. Preparation of sample: Before GPC analysis, the drayed sample was dissolved in THF, passed through a neutral alumina column and PTFE 0.2 μm filter, and dried under vacuum for 1 day. The final product was characterized by GPC, prepared a sample with concentration 5 mg/ml in THF [17].

Chromatography (GPC) is a type of size exclusion chromatography (SEC), which separates the analytes according to size, typically in organic solvents, which is perfect for the job being done. The technique is often used for the analysis of polymers since it has great advantages and allows the determination of values that are very precise.

5.3.3. Determination of theorical mass

To determine the theoretical molecular mass of the sample it is necessary to perform the following calculations:

To make this calculation, it is necessary to first know the conversion since that way we will know how much polymer has been formed. The DP, which is the amount that must be formed of polymer in the case that the conversion is 100%, is multiplied by the conversion.

Finally, this value is multiplied by the number of monomer molecules that have reacted (DP_{th}) and the molecular mass of the initiator is added.

$$M_{n,th} = \frac{[LIM]_o}{[EBiB]_o} \cdot conv \cdot M_{LIM} + M_{EBiB}$$

- $M_{n,th}$ - Theoretical molecular mass
- $[LIM]_o$ - Monomer concentration
- $[EBiB]_o$ - Initiator concentration
- conv - Conversion of monomer
- M_{LIM} - Monomer molecular mass
- M_{EBiB} - Initiator molecular mass

5.4. RESULTS

Subsequently, the data obtained during the experiment was analysed, so that conclusions can be drawn from them, but to get a reaction that is correct we first need to know the potential that needs to be applied in the reaction. To achieve this, the cyclic voltammetry (CV) analysis must be performed:

This technique is of great importance in the field of electrochemistry, especially in studies where redox processes are used. Through relatively simple and rapid tests it is possible to obtain an important set of information.

To carry out this technique, a potential sweep is applied to the working electrode in the forward and backward directions, the signal caused is triangular. There are four important values: the initial and final potential E_o, E_f, the cut potential of the anode E_a and the cut potential of the cathode E_c. The current intensity flowing through the electrode is measured. The intensity that is measured is a function of the applied potential and the concentration of the electroactive species.

The applied potential varies linearly from E_o to E_f, then the direction of the current is reversed and returns to its original value E_o. The most important variables in this type of study are the structure of the organic molecule, the polymer, the support of the electrolyte, the pH, the potential of the electrode and the temperature.

The choice of an appropriate applied potential (E_{app}) is the most importance when using controlled potential preparative electrolysis. The cyclic voltammetry was conducted the cathodic potential was determined. The value of cathodic potential was appropriated to determining appropriate applied potential conduct reactions.

Using a correct (E_{app}) value is very important because with it you can control that the amount of catalytic complex that is acting on the polymerization remains constant and everything is not deactivated. In this way the reaction speed can be controlled [18][19].

Cyclic voltammetry was performer in DMF solution. According to previous measures E_{pc} in miniemulsion is 50 mV more negative than in DMF solution, therefore it is established as E_{pc} = -50 mV -150 mV = -200 mV

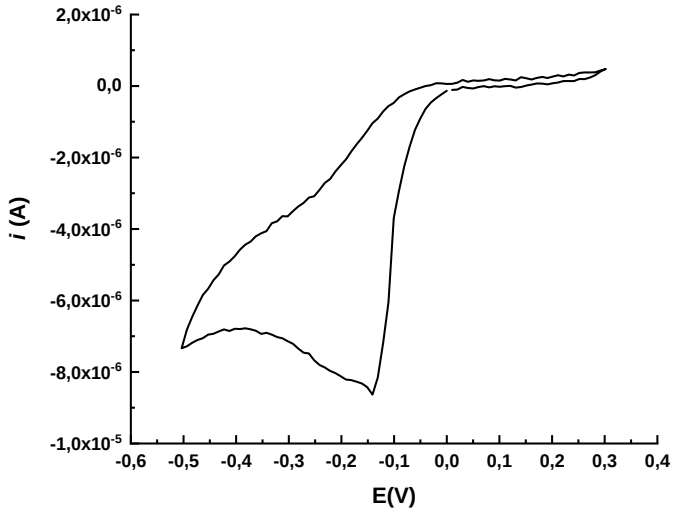

Figure 17: Cyclic Voltammetry (CV) graph

During the polymerization, the following reaction occurs:

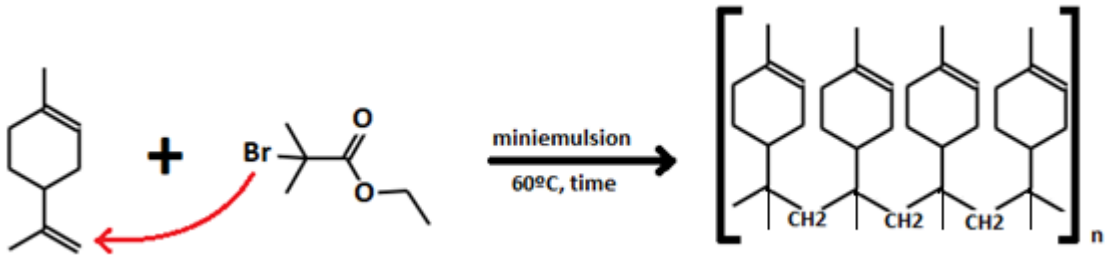

Figure 18: Scheme of polymerization of limonene.

As it can see, the reaction starts with the initiator, which can break the limonene double bond, after that that limonene chain reacts with the next one so that polymerization is generated. When this process ends, there is a limonene polymer that has the bromine atom at the end of the chain.

The catalyst helps the reaction to take place and form more quickly and controlled, reducing the activation energy. For this reason, it is important to find a technique that regenerates the catalyst so that it can be used constantly without deactivation.

5.4.1. Reaction 1

During electrochemically mediated polymerization, the resulting current was recorded. At the beginning of the electrolysis, only deactivator was present in the reaction mixture, so the cathodic current decayed was converted to the activator. Subsequently, the current approached low and constant value as the radio, adjusted by the selected applied potential, was obtained. A more negative potential generated larger initial value of the current indicating a higher reduction rate and thus faster polymerization. This is due the quicker regeneration of the activator and resulting higher concentration of the radical species.

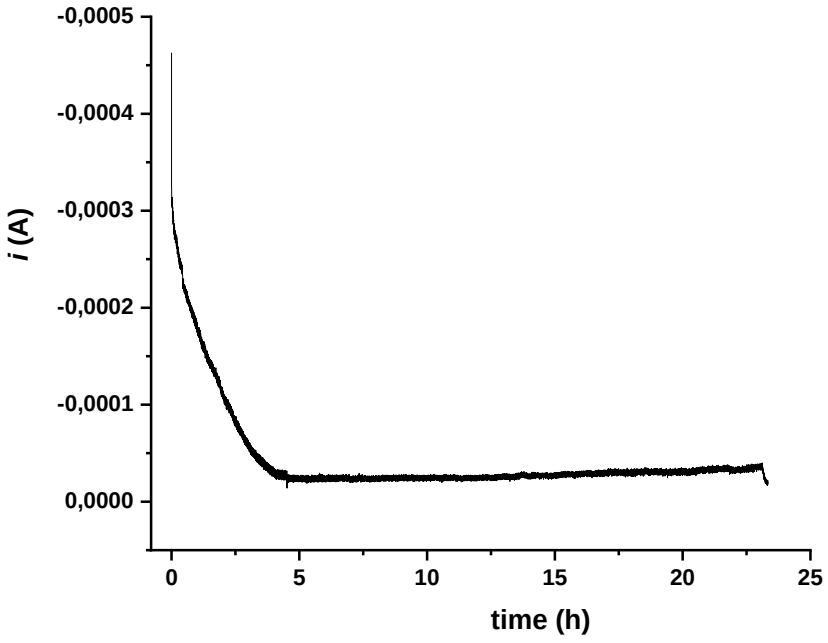

Figure 19: Ratio intensity time for reaction 1.

Thanks to this graph, the values of Q and e can be easily calculated. Q is total electric charge that passes through the system during the reaction, it is measured as filed under graph. In the case of reaction 1 a value of (-) 3.71 C was obtained.

Regarding the value e, which is the number of electrons that move during the reaction, the 0.038 mmol was obtained, using the following expression:

$$e = \frac{Q}{F} \cdot 1000$$

Where the value of F is 96485 [C/mol] being the constant of Faraday.

For reaction 1 the following expression is applied, and in this way the value of the applied potential is obtained.

$$E_{app} = E_{pc} - 100\,mV = -300mV$$

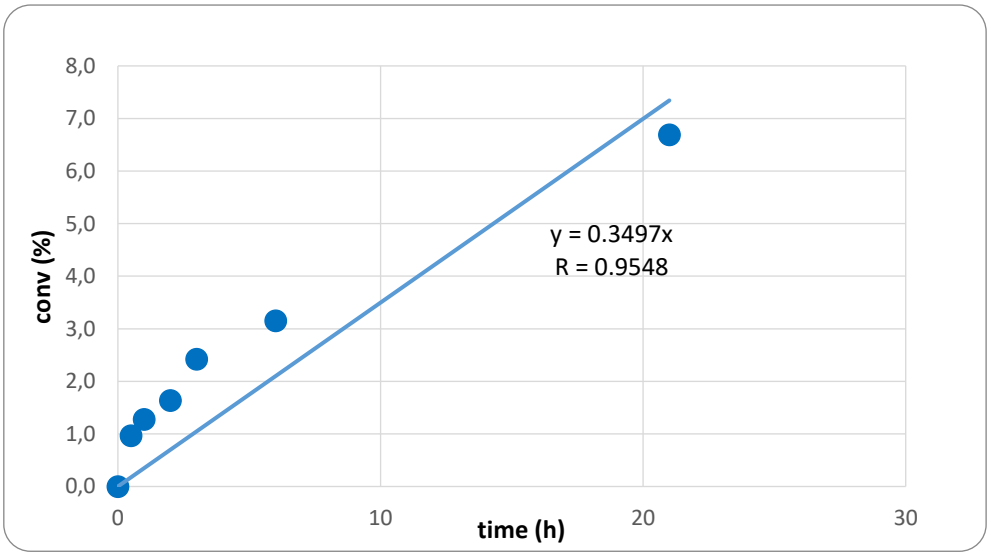

Figure 20: Graph of dependence of polymerization time monomer conversion, reaction 1.

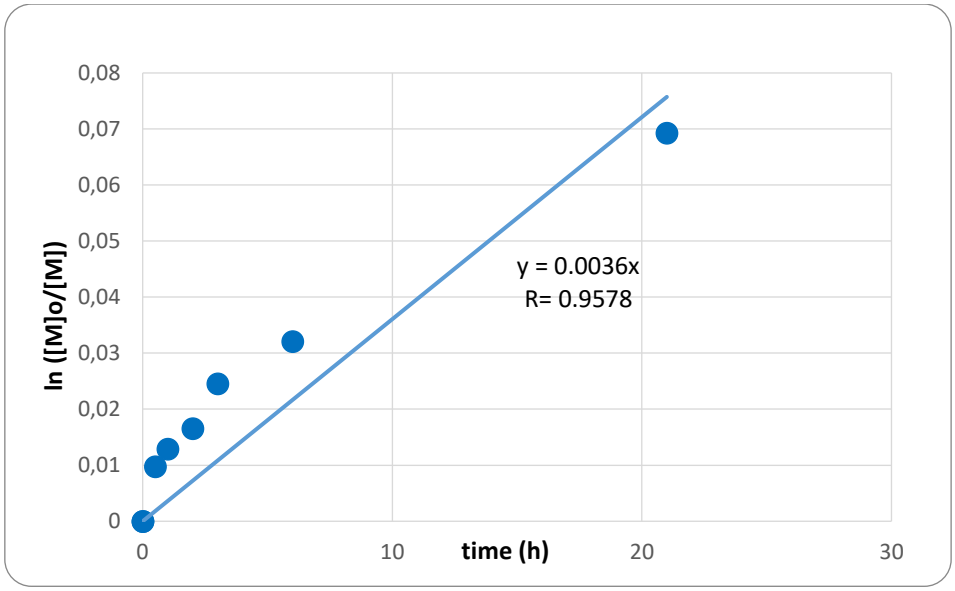

Figure 21: Graph of dependence ln ([M]o/[M]) on the time of polymerization, reaction 1.

As shown in Figure 20, the conversion advances linearly with time of reaction, but it can be highlighted that at the beginning the rate of polymerization was higher. In this reaction the conversion speed was slow since at 20 hours a conversion of approximately 7% is obtained, this is a consequence of small reduction of electrochemical potential which was applied. The linear relationship of ln $[M]_0/[M]$ on the time of polymerization is presented results from a constant concentration of propagating radicals during the reaction and indicates its controlled course.

5.4.2. Reaction 2

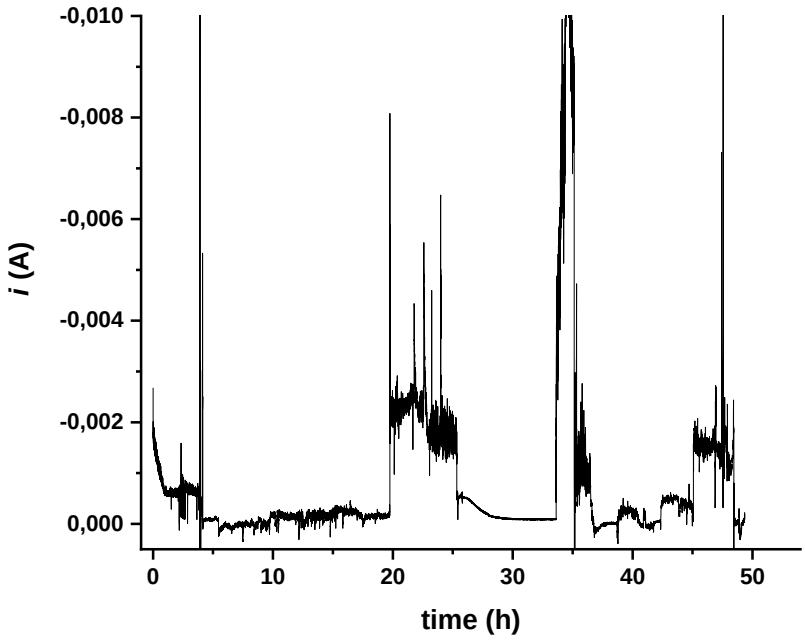

Figure 22: ratio intensity time for reaction 2

In the case of reaction 2 the values that have been obtained are the following: the total charge that the reaction passes through (Q) is equal at -137.4 C, which pose 1.42 mmol of charge. They were obtained applying the same considerations as in the case of reaction 1.

For reaction 2 the following expression is applied, and in this way the value of the potential to be applied can be obtained [12].

$$E_{app} = E_{pc} - 200\,mV = -400mV$$

By applying a higher potential in reaction 2, the equipment captures a greater amount of noise. However, the number of electrons that pass through the reaction is greater in the case of the second reaction. But in addition to that, noise can come from:

1. The working electrode (WE) may have been touched by the counter electrode (CE).
2. During the reaction, some air has been introduced into the setup and oxygen is rapidly reduced
3. In the total load, the side reactions have a predominant role since the reaction has a radical character.

To know if the control of the reaction is lost, it is necessary to know the molecular weight distribution value, if this value is too large, the control is lost.

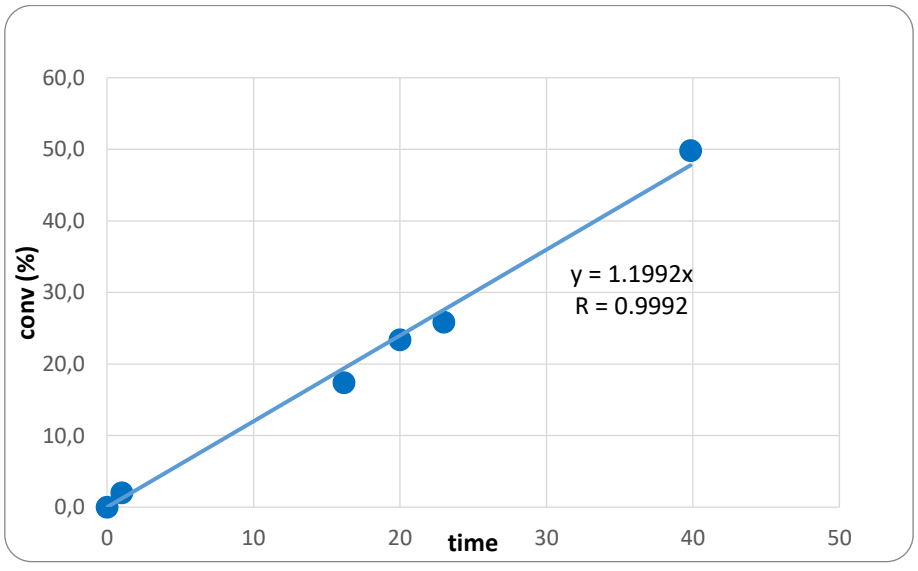

Figure 23: Graph of dependence of polymerization time monomer conversion, reaction 2.

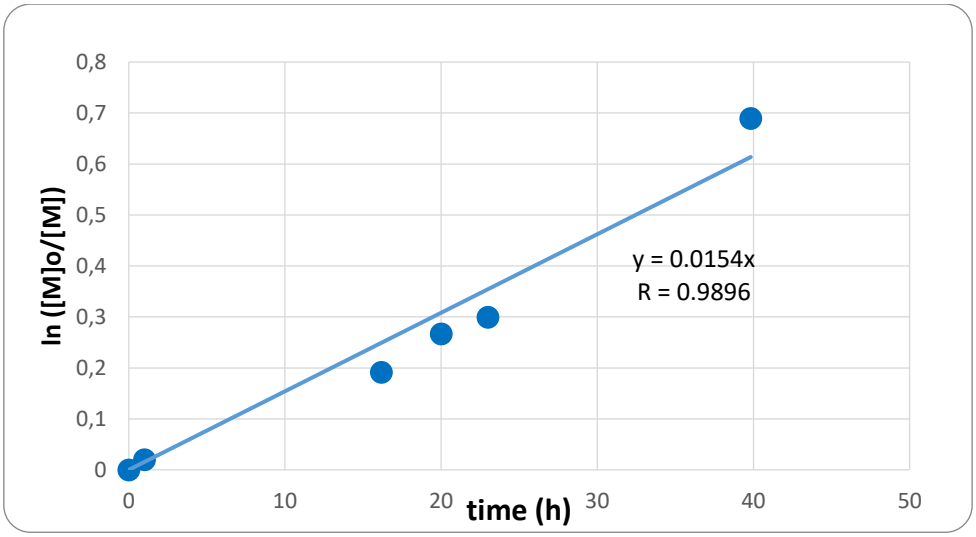

Figure 24: Graph of dependence ln ([M]o/[M]) on the time of polymerization, reaction 2.

The linear relationship of $\ln[M]_0/[M]$ on the time of polymerization presented in Figure 34 results from a constant concentration of propagating radicals during the reaction time what indicates its controlled course. Knowing the first-order reaction plot, the value of the speed constant for the two reactions can be easily deduced, which coincides with the slope of the line. The numerical values of the two reactions that define them mathematically are reflected in the following section.

5.4.3. Results comparison

Next, the results obtained in the two reactions that have taken place will be compared. At the top are the values belonging to the first reaction and at the bottom are those of the second. *Table 7: Experimental results*.

[LIM]/[EBiB]/ [$Cu^{II}Br_2$/TPMA]	time (h)	DP_{th}	Conv (%)	$M_{n,th}$	MW (GPC)	MWD (GPC)	Cat.Complex (ppm)	E_{app} (mV)	$k_p^{app}(h^{-1})$
200/1/0.1	21.00	13.40	6.70	1107	983	1.02	500	- 300	0.0036
200/1/0.2	39.83	99.70	49.80	6984	48854	2.03	1000	- 400	0.0150

k_p^{app} – First order reaction rate constant.

α – Monomer conversion.

DP_{th}– Theoretical degree of polymerization

MW – Molecular weight obtained.

MWD – Molecular weight distribution

E_{app} – Appropriate applied potential.

$M_{n,th}$– Theoretical molecular mass.

It can be seen how the amount of catalyst used in reaction 2 is higher and applied potential is more negative. This will modify the results obtained.

Firstly, the degree of polymerization obtained is much greater in the case of reaction 2, this will be reflected in the rest of the parameters such as molecular weight.

Additionally, with twice the amount of catalyst in solution and more negative applied potential the reaction rate is also faster [20], however, the molecular weight distribution value indicates that there is a greater dispersion in the reaction, that is, control over the polymerization has been lost partly.

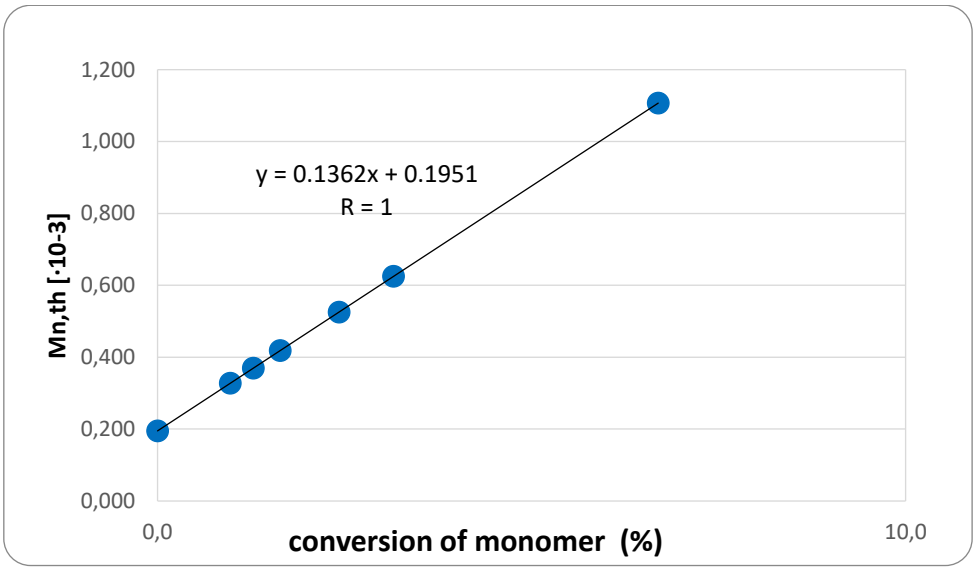

Figure 25: Graph of the theoretical dependence of the polymer molecular weight on the monomer conversion, reaction 1.

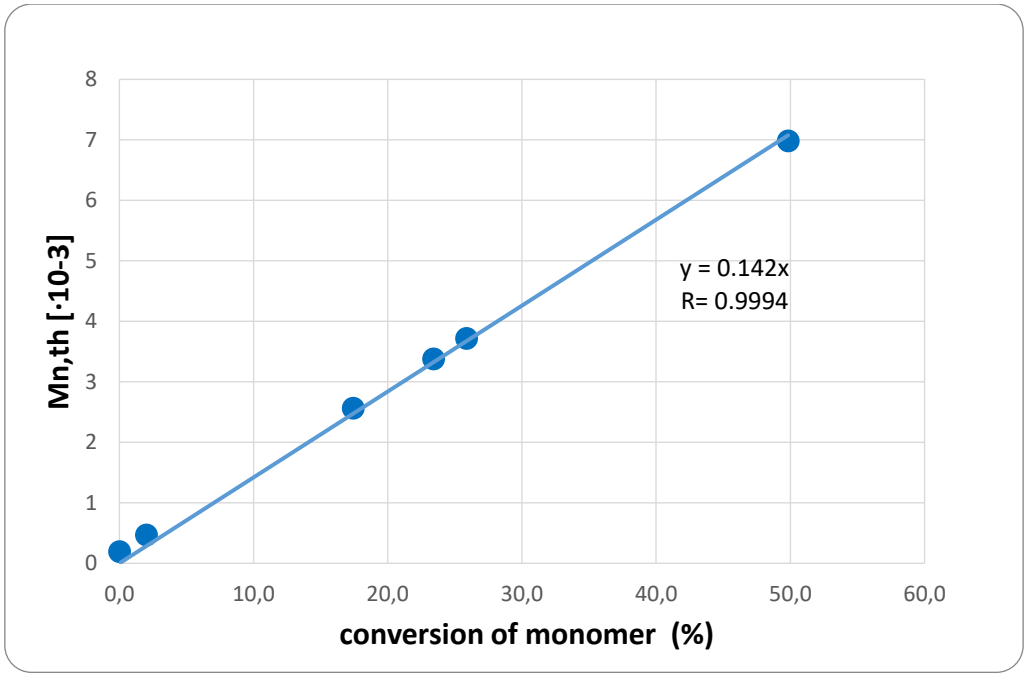

Figure 26: Graph of the theoretical dependence of the polymer molecular weight on the monomer conversion, reaction 2.

From the previous figures it can be said that the control over the polymerization is maintained since the concentration of the radicals is constant. In addition, it is observed that the reaction that had a higher catalyst load and more negative value of applied potential (reaction 2) was faster, and the monomer conversion was higher.

6. CONCLUSIONS

Synthesis of poly (D-limonene) was carried out using the *se*ATRP miniemulsion technique. Polymerization reactions were carried out at two different potential values. The aim of the study was to determine the impact of the applied electrochemical potential on the course of the reaction, as well as to assess the possibilities of controlling over the process.

1. Shifting the value of the applied electrochemical potential towards more negative results in an increase in the polymerization rate due to the faster reduction rate of the deactivator to the form of an activator, and thus a higher concentration of propagating radicals.
2. 2. The resulting low monomer conversion value results from driving the reaction to a low catalyst concentration of 500 ppm with positive applied electrochemical potential.
3. The linear relationship of $\ln[M]_0/[M]$ on the time of polymerization indicates a constant concentration of propagating radicals in the analysed process, and thus the controlled course of the reaction.
4. The most important role in *se*ATRP in the miniemulsion is the hydrophilic nature of the catalyst and the anionic surfactant, which changes the surface tension of the liquid, affecting the course of polymerization. The coexistence of interfacial and ion-pair catalysis allows the process to be controlled without the necessity for a double hydrophilic - hydrophobic catalytic system.
5. The application of water as mild solvent is used for one of the phases. Reactions conducted in miniemulsion environment are efficient and functional and pose a perfect way for eco-friendly polymer industry. Therefore, this technique is good to be used in polymerization processes that want to respect the environment and create complex chains with small molecular weight distributions.

7. BIBLIOGRAPHY

- [1] Matyjaszewski K. Atom Transfer Radical Polymerization (ATRP): Current Status and Future Perspectives, *Macromolecules* 2012, 45, 10, 4015.
- [2] Wang Y., Lorandi F., Fatin M., Chmielarz P., A. Isse A., Gennaro A., Matyjaszewski K., Miniemulsion ARGET ATRP via Interfacial and Ion-Pair Catalysis: From ppm to ppb of Residual Copper, *Macromolecules* 2017, 50, 8417.
- [3] Chern, C.S., Emulsion Polymerization Mechanisms And Kinetics, *Progress in Polymer Science* 2006, 31, 443.
- [4] Wang, y., Kwak, Y., Buback, J., Buback, M., Matyjaszewski, K., Determination of ATRP Equilibrium Constants under Polymerization Conditions, *ACS Macro Letters* 2012, 1, 1367.
- [5] Ouchi, M., Terashima, T., Sawamoto, M., Transition Metal-Catalyzed Living Radical Polymerization: Toward Perfection in Catalysis and Precision Polymer Synthesis, *Chemical Review* 2009, 109, 4963.
- [6] Wang, S.T., Schork, F.J., Poehlein, G.W., Gooch, J.W., Emulsion and Miniemulsion Copolymerization of Acrylic Monomers in the Presence of Alkyd Resin, *Journal of Applied. Polymer Science* 1996, 60, 2069.
- [7] Zaborniak, I., Chmielarz, P., Temporally Controlled Ultrasonication-Mediated Atom Transfer Radical Polymerization in Miniemulsion. *Macromolecular Chemistry and Physics* 2019, 220, 1900285.
- [8] Fantin M., Chmielarz P., Wang Y., Lorandi F., Isse A., Gennaro A., Matyjaszewski K., Harnessing the Interaction between Surfactant and Hydrophilic Catalyst To Control *e*ATRP in Miniemulsion, *Macromolecules* 2017, 50, 3726.
- [9] Kamigaito, M., Ando, T., Sawamoto, M., Metal-Catalyzed Living Radical Polymerization, *Chemical Reviews* 2001, 101, 3689.
- [10] Schroeder, H., Lake, B., Demeshko, S., Shaver, M., Buback, M., A Synthetic and Multispectroscopic Speciation Analysis of Controlled Radical Polymerization Mediated by Amine–Bis(phenolate)iron Complexes, *ACS MacroLetters* 2015, 48, 4329.
- [11] Fantin M., Park S., Matyjaszewski K., Wang Y., Electrochemical Atom Transfer Radical Polymerization in Miniemulsion with a Dual Catalytic System, *Macromolecules* 2016, 49, 8838.

- [12] Dong, H., Mantha, V., Matyjaszewski, K., Thermally Responsive $PM(EO)_2MA$ Magnetic Microgels via Activators Generated by Electron Transfer Atom Transfer Radical Polymerization in Miniemulsion, *Chemistry of Materials* 2009, 21, 3965.
- [13] Chmielarz, P., Synthesis of High Molecular Weight Five-Arm Star Polymers by Improved Electrochemically Mediated Atom Transfer Radical Polymerization, *Polimery* 2017,62, 42.
- [14] Bechthold, N., Tiarks, F., Willert, M., Landfester, K., Antonietti, M., Miniemulsion Polymerization: Applications And New Materials, *Macromolecular Symposia* 2000, 151, 1.
- [15] Averick, S., Simakova, A., Park, S., Konkolewicz, D., Magenau, A., Mehl, R., Matyjaszewski, K., ATRP under Biologically Relevant Conditions: Grafting from a Protein, *ACS Macro Letters* 2012, 1, 6.
- [16] Landfester K. Miniemulsion Polymerization and The Structure of Polymer and Hybrid Nanoparticles. *Angewandte Chemie International Edition,* 2009; 48, 4488.
- [17] Van Steenberge, P., D´hooge, D., Wang, Y., Zhong, M., Reyniers, M., Konkolewicz, D., Matyjaszewski, K., Marin, G., Linear Gradient Quality of ATRP Copolymers, *Macromolecules* 2012, 45, 8519.
- [18] Prieto, J., (2020) Voltametría Cíclica Recovered from: https://bsginstitute.com/bs-campus/blog/voltametria-ciclica-109
- [19] Chmielarz, P., Krys, P., Wang, Z., Wang, Y., Matyjaszewski, K., Synthesis of well-defined polymer brushes from silicon wafers *via* surface-initiated *se*ATRP, *Macromolecular Chemistry and Physics* 2017, 218, 1700106.
- [20] Krys, P., Ribelli, T., Matyjaszewski, K., Gennaro, A., Relation between Overall Rate of ATRP and Rates of Activation of Dormant Species, *Macromolecules* 2016, 49, 2467.

POLITECHNIKA RZESZOWSKA
Wydział Chemiczny
Zakład Chemii Fizycznej

Rzeszów, 22 czerwca 2020

STRESZCZENIE PRACY DYPLOMOWEJ MAGISTERSKIEJ

Badania nad polimeryzacją rodnikową z odwracalną dezaktywacją

Autor: inż. Ramón Peña
Opiekun: dr hab. inż. Paweł Chmielarz, prof. PRz
Słowa kluczowe: eATRP, poli(D-limonen), analiza grawuimetryczna, GPC
Streszczenie:

Głównym celem badań jest optymalizacja syntezy homopolimerów poli(D-limonenu) w układzie miniemulsji. Reakcje prowadzono za pomocą polimeryzacji rodnikowej z przeniesieniem atomu (ATRP), w której aktywatory regenerowane są w skutek przepływającego ładunku elektrycznego (*e*ATRP). Metoda ta pozwala na jednoczesny wzrost wszystkich łańcuchów przy zachowaniu dobrej kontroli nad właściwościami fizykochemicznymi łańcuchów polimerowych. W pracy przeanalizowana została również kinetyka i wyznaczone zostały stałe szybkości reakcji polimeryzacji na podstawie analizy grawimetrycznej i GPC.

RZESZÓW UNIVERSITY OF TECHNOLOGY
Faculty of Chemistry
Department of Physical Chemistry

Rzeszów, 22 June 2020

MSc DIPLOMA THESIS ABSTRACT

Study of Reversible-Deactivation Radical Polymerization

Author: Ramón Peña, Eng.
Supervisor: Paweł Chmielarz, DSc, PhD, Eng., Associate Prof.
Keywords: eATRP, poly(D-limonene), gravimetric analysis, GPC
Abstract:

The headline aim of the research is the optimization of the synthesis of poly(D-limonene) homopolymers in miniemulsion system. Reactions were conducted using Atom Transfer Radical Polymerization (ATRP) technique, controlled by electrical current (*e*ATRP). This technique allows for simultaneous growth of all chains affording good control over the physicochemical properties of polymers. In this work, the kinetic was also analyzed and the rate constants of polymerization reactions based on gravimetric and GPC analysis were determined.