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# Synthesis and development of tailor-made nanoparticles for advanced coatings

Master's Thesis in Chemical Engineering submitted to the Department of  
Chemical Engineering, Faculty of Science and Technology, University of Coimbra

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UNIVERSIDADE DE COIMBRA



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# Synthesis and development of tailor-made nanoparticles for advanced coatings

Master's Thesis in Chemical Engineering, supervised by Professor Jorge Coelho and submitted to the Department of Chemical Engineering, Faculty of Science and Technology, University of Coimbra

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UNIVERSIDADE DE COIMBRA



“It always seems impossible until it’s done.”

**Nelson Mandela**



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## Abstract

The purpose of this work was the synthesis of well-defined linear block copolymers of different molecular weights, with both ionic and non-ionic functional groups to disperse and stabilize TiO<sub>2</sub> particles in aqueous medium, which would be used in paint formulations.

Synthesis of block copolymers with controlled structure and different molecular weight required in this work has been made by ATRP. PAMPTMA-*b*-POEOA block copolymers has been synthesized during this work. One block (AMPTMA) will anchor on the pigment surface promoting electrostatic stabilization, while the block with affinity to the aqueous medium (OEOA) will promote the steric stabilization avoiding flocculation.

After the synthesis, DLS and  $\zeta$  potential test has been done to the copolymers. All the block copolymers present promising results in these tests, with hydrodynamic diameters between 200 and 245 nm after 5 days, and  $\zeta$  potential above 40 mV. Also, a positive relation between the molecular weight of the OEOA block and the hydrodynamic diameter of the particles has been observed.

The copolymers samples have also been tested in a paint formulation. However, PAMPTMA<sub>85</sub>-*b*-POEOA<sub>14</sub> have turned into a gel when Texanol (ester) was added to the paint formulation. Moreover, 48 hours after the paint formulation production, PAMPTMA<sub>52</sub>-*b*-POEOA<sub>39</sub> sample has turned into a gel. All the tested copolymers samples are more viscous than the reference and a positive relation between the copolymer molecular weight and the viscosity has been observed.

PAMPTMA<sub>30</sub>-*b*-POEOA<sub>28</sub> have a similar behavior to the reference regarding to the paint brightness, CIELab parameters and contrast ratio. Also, PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> presented similar results to the reference regarding CIELab parameters and contrast ratio. However, PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> have shown better brightness than the reference when tested in a paint formulation, indicating that this copolymer disperses better the pigment particles. Also, in the DLS test the same copolymer have exhibited similar values to the reference.

The samples have turned into a gel after being stored for 28 days, indicating that the samples cannot provide stability over time as TiO<sub>2</sub> pigment stabilizers.

For the future, it would be relevant to synthesize different block copolymers having one segment of PAMPTMA or POEOA to study their differences and compare with the copolymer synthesized in this work. For example, synthesize mPEG-*b*-PAMPTMA to study the difference between the hydrophilic groups or PAETAC-*b*-POEOA and mPEG-*b*-PAETAC to compare with AMPTMA and to evaluate the difference between OEOA and PEG chain block.

**Keywords:** block copolymers, ATRP, TiO<sub>2</sub>, aqueous dispersion, polymeric dispersants.



## Resumo

Este trabalho tem por objectivo a síntese de copolímeros de bloco de diferentes pesos moleculares com grupos iónicos e não-iónicos para dispersar e estabilizar partículas de  $\text{TiO}_2$  em meio aquoso. Subsequentemente, esta formulação tem por objectivo ser utilizada numa formulação de tinta.

A síntese dos copolímeros de bloco com estrutura controlada e diferentes pesos moleculares requerida neste trabalho foi feita por ATRP. Ao longo deste trabalho foram sintetizados copolímeros de bloco PAMPTMA-*b*-POEOA em que o bloco de AMPTMA irá adsorver à superfície das partículas dos pigmentos e promover estabilização electrostática enquanto o bloco com afinidade para o meio aquoso (OEOA) irá promover estabilização estérea para prevenir a ocorrência de floculação.

Após a síntese os copolímeros foram sujeitos a testes de DLS e Potencial Zeta. Nestes testes todos eles apresentaram resultados promissores com diâmetros hidrodinâmicos entre os 200 e 245 nm após 5 dias de teste e um potencial zeta superior a 40mV. Também foi verificado uma relação positiva entre o peso molecular do bloco de OEOA e o diâmetro hidrodinâmico das partículas.

Os copolímeros foram também testados após serem incorporados numa formulação de tinta. No entanto, durante a produção da formulação de tinta o copolímero PAMPTMA<sub>85</sub>-*b*-POEOA<sub>14</sub> gelificou aquando da incorporação de Texanol (éster) na referida formulação. Ainda, a amostra que continha o copolímero PAMPTMA<sub>52</sub>-*b*-POEOA<sub>39</sub> gelificou 48 horas após a produção da referida formulação. Todas as amostras de copolímeros testadas demonstraram uma viscosidade superior à referência e uma relação positiva entre o peso molecular do polímero e a sua viscosidade.

Quanto ao copolímero PAMPTMA<sub>30</sub>-*b*-POEOA<sub>28</sub>, este apresentou um comportamento semelhante à referência em relação aos parâmetros CIELab, brilho e contraste. Também o copolímero PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> apresentou um comportamento semelhante à referência em relação ao contraste e aos parâmetros CIELab. No entanto, esta amostra apresentou melhores resultados que a referência em relação ao brilho, em especial no brilho a 60°, indicando uma melhor dispersão das partículas de pigmento. Também no teste DLS, a amostra PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> apresentou valores semelhantes à referência.

Todas as amostras gelificaram durante o teste de estabilidade ao armazenamento indicando que as amostras não conseguem estabilizar ao longo do tempo os pigmentos de  $\text{TiO}_2$ .

No futuro seria relevante sintetizar copolímeros de bloco com um segmento de PAMPTMA ou um segmento de OEOA para comparar e estudar as diferenças com o copolímero de bloco sintetizado neste trabalho. Por exemplo, sintetizar mPEG-*b*-PAMPTMA para estudar as diferenças entre o grupo hidrofílico ou PAETAC-*b*-POEOA e mPEG-*b*-PAETAC para comparar com o grupo AETAC com o grupo de AMPTMA e para estudar as diferenças entre o bloco de OEOA e o bloco de PEG.

**Palavras-chave:** copolímeros de bloco, ATRP,  $\text{TiO}_2$ , dispersão aquosa, dispersantes poliméricos.



# Table of Contents

1. Introduction.....	1
1.1 Background and Objectives.....	1
2. State of the art.....	3
2.1 Paints and coatings .....	3
2.2 Pigments .....	4
2.2.1 Titanium dioxide (TiO <sub>2</sub> ).....	5
2.3 Particles stabilization.....	6
2.4 Polymeric Dispersants .....	7
2.5 Reversible-deactivation radical polymerization (RDRP).....	9
2.5.1 Atom Transfer Radical Polymerization (ATRP) .....	10
2.6 Block copolymers.....	11
2.6.1 Copolymers characterization.....	13
2.7 Adsorbed polymer conformation.....	14
3. Experimental.....	17
3.1 Materials.....	17
3.2 Synthesis.....	17
3.2.1 PAMPTMA.....	17
3.2.2 PAMPTMA- <i>b</i> -POEOA.....	18
3.3 Characterization.....	18
3.3.1 Size Exclusion chromatography (SEC).....	18
3.3.2 Nuclear Magnetic Resonance ( <sup>1</sup> H-NMR Spectra) .....	19
3.3.3 Dynamic Light Scattering (DLS) and Zeta Potential measurements .....	19
4. Results and Discussion .....	21
4.1 Block copolymers characterization .....	21
4.2 Dynamic Light Scattering (DLS) .....	25
4.3 Zeta Potential.....	27
4.4 Paint Formulation Performance.....	28
5. Conclusions and Future Works.....	31
5.1 Conclusions .....	31
5.2 Future Work .....	31
6. References.....	33
Appendix A – Monomers <sup>1</sup> H NMR spectra.....	36
Appendix B – Copolymers <sup>1</sup> H NMR spectra.....	38
Appendix C – DLS samples.....	41



## List of Figures

<b>Figure 1.</b> Stabilization mechanisms in particle suspensions. (Farrokhpay, 2009).....	7
<b>Figure 2.</b> Stabilized system (a). “Bridging” flocculation (b) Depletion flocculation (c). Adapted from (Myers, 1999) .....	7
<b>Figure 3.</b> ATRP equilibrium. (Matyjaszewski, 2012).....	10
<b>Figure 4.</b> General mechanism of SARA ATRP mediated by Cu(0) and Cu(II)X <sub>2</sub> . (Mendonça et al., 2014) .....	11
<b>Figure 5.</b> Schematic representation of polymer system. Adapted from (Matyjaszewski & Tsarevsky, 2009).....	12
<b>Figure 6.</b> Schematic representation of polymer architecture. Adapted from (Matyjaszewski & Tsarevsky, 2009).....	12
<b>Figure 7.</b> P(AMPTMA)-b-P(OEOA) chemical structure.....	13
<b>Figure 8.</b> Schematic representation of adsorbed polymer molecule at the solid–liquid interface. (Farrokhpay, 2009).....	15
<b>Figure 9.</b> Conversion vs. time for the SARA ATRP of AMPTMA.....	22
<b>Figure 10.</b> <sup>1</sup> H NMR spectra of PAMPTMA in D <sub>2</sub> O. Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments. ....	23
<b>Figure 11.</b> <sup>1</sup> H NMR spectrum of PAMPTMA <sub>52</sub> -b-POEOA <sub>39</sub> in D <sub>2</sub> O. Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments.....	24
<b>Figure A.1.</b> 1H NMR spectrum of AMPTMA in D <sub>2</sub> O. Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments. ....	36
<b>Figure A.2.</b> 1H NMR spectrum of OEOA in D <sub>2</sub> O. Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments. ....	37
<b>Figure B.1.</b> 1H NMR spectrum of PAMPTMA <sub>38</sub> -b-POEOA <sub>36</sub> in D <sub>2</sub> O. Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments. ...	38
<b>Figure B.2.</b> 1H NMR spectrum of PAMPTMA <sub>30</sub> -b-POEOA <sub>28</sub> in D <sub>2</sub> O. Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments. ...	39
<b>Figure B.3.</b> 1H NMR spectrum of PAMPTMA <sub>85</sub> -b-POEOA <sub>14</sub> in D <sub>2</sub> O. Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments. ...	40
<b>Figure C.1.</b> Photos of TiO <sub>2</sub> suspensions on the 5th day. From left to right: PAMPTMA <sub>85</sub> -b-POEOA <sub>14</sub> , PAMPTMA <sub>38</sub> -b-POEOA <sub>36</sub> , PAMPTMA <sub>30</sub> -b-POEOA <sub>28</sub> , TiO <sub>2</sub> , PAMPTMA <sub>52</sub> -b-POEOA <sub>39</sub> , Additol VXW 6200. ....	41





## List of Tables

<b>Table 1.</b> Composition of paints. Adapted from (Lambourne & Strivens, 1999).....	3
<b>Table 2.</b> $M_n$ determined by SEC and $^1\text{H}$ NMR and $M_w/M_n$ determined by SEC for the synthesized polymers.....	21
<b>Table 3.</b> $D_h$ , PDI and attenuator values of block copolymers and their reference determined by DLS without the presence of $\text{TiO}_2$ particles. ....	25
<b>Table 4.</b> $D_h$ , PDI and attenuator values of block copolymers and their reference determined by DLS in the presence of $\text{TiO}_2$ particles during 5 days.....	26
<b>Table 5.</b> Copolymers and Additol zeta potential values in the absence of $\text{TiO}_2$ particles.....	27
<b>Table 6.</b> Copolymers and Additol VXW 6200 zeta potential variation in the presence of $\text{TiO}_2$ particles. ....	28
<b>Table 7.</b> Properties of a paint formulation containing different polymers as stabilizing agent. ....	29



## Acronyms and Nomenclature

$\mu\text{mol}$	Micromole
2VP	2-Vinylpyridine
4VP	4-Vinylpyridine
$\text{Al}_2\text{O}_3$	Aluminium Oxide
$\text{AlCl}_3$	Aluminium Chloride
AMPTMA	(3-acrylamidopropyl)trimethylammonium Chloride
ATRP	Atom Transfer Radical Polymerization
Att.	Attenuator
Co	Cobalt
Cu	Copper
$\text{CuCl}_2$	Copper(II) Chloride
$D$	Dispersity Index
$\text{D}_2\text{O}$	Deuterium Oxide
$D_h$	Hydrodynamic Diameter
DLS	Dynamic Light Scattering
DMAEMA	2-(dimethylamino)ethyl methacrylate
DP	Degree of polymerization
ECP	Ethyl 2-Chloropropionate
Fe	Iron
g	Grams
h	Hours
HCl	Chloridric Acid
iep	Isoelectric Point
J	Joule
KU	Krebs Units
$M_0$	Molecular Weight of the Repeating Unit
MANa	Sodium methacrylate
$\text{Me}_6\text{TREN}$	Tris[2-(dimethylamino)ethyl]amine
MeOH	Methanol
mg	Milligrams
MHz	Megahertz
mL	Milliliter
mmol	Millimole
$M_n$	Number-average Molecular Weight
Mo	Molybdenum
Mol	Mole
mPa	Millipascal
mPEG	Poly(ethylene glycol) methyl ether
mV	Millivolt
MW	Molecular Weight

$M_w$	Weight-average Molecular Weight
MWD	Molecular Weight Distribution
N	Nitrogen
NaPAA	Sodium Polyacrylate
Ni	Nickel
nm	Nanometer
NMP	Nitroxide-Mediated Polymerization
NMR	Nuclear Magnetic Resonance
°C	Degree Celsius
OEOA	Poly(ethylene glycol) methyl ether
Os	Osmium
P	Poise
P2VP	Poly(2-Vinylpyridine)
P4VP	Poly(4-Vinylpyridine)
PAA	Polyacrylate
PAMPTMA	Poly((3-acrylamidopropyl)trimethylammonium chloride)
Pd	Palladium
PDI	Polydispersity Index
PDMAEMA	Poly(2-(dimethylamino)ethyl methacrylate)
POEOA	Poly(ethylene glycol) methyl ether
PTFE	Polytetrafluoroethylene
RAFT	Reversible Addition-Fragmentation Chain Transfer
RDRP	Reversible-deactivation radical polymerization
Re	Rhenium
Rh	Rhodium
RI	Refractive index
rpm	Revolutions per minute
Ru	Ruthenium
s	Second
SARA ATRP	Supplemental Activator and Reducing Agent Atom Transfer Radical Polymerization
SEC	Size Exclusion Chromatography
SiO <sub>2</sub>	Silicon Dioxide
TEM	Transmission Electron Microscopy
Ti	Titanium
TiO <sub>2</sub>	Titanium Dioxide
TMS	Tetramethylsilane
ζ	Zeta

# 1. Introduction

## 1.1 Background and Objectives

Paints and coatings play an important role in the cultural humanity history. The history of paint dates back to pre-historic era whereas natural pigments like ochre, hematite or brown iron ore were used to decorate the cave walls. Paints were used to express thoughts, emotions, and the culture of the people. Later in Europe, a formulation of limestone and water has started to being used in houses to improve the weatherability and for aesthetic reasons, and even now, paints are used for those reasons. Presently, pigments are one of the basic and most important ingredients in paint formulations.

Solvent, ligand, pigments and additives are the four main components of paints. (Carranquina, 2011) Titanium dioxide ( $\text{TiO}_2$ ) pigment is being widely used in industries like plastic, pharmaceutical, papermaking or paint, and nowadays is considered the most important white pigment used in the world. A good pigment dispersion in paints is indispensable because it will affect durability during outdoor exposure, gloss, opacity or colour distribution, but also for economic reasons. (Farrokhpay, 2009)

Over the last years, associated to the scientific knowledge, paint formulation regulations, environmental restrictions and technological development, the paint industry has strongly invested in products with less impact on the environment and human health, preferring aqueous dispersions to non-aqueous ones. These concerns have promoted an intense development of water-based products. (Herbst & Hunger, 2004) The raising environmental concerns have created a problem in the paint industry, since water-based products have a higher pigment aggregation and the complete dispersion of pigments in this medium is difficult to achieve. Besides that,  $\text{TiO}_2$  is water insoluble, which cause particles flocculation, affecting important end-use properties of the pigment.

In order to enhance the  $\text{TiO}_2$  dispersion, the industry uses different strategies. One involves the surface modification of titania pigment with alumina to control crystal structure and regulate agglomeration, decreasing the effect of the Van der Waals attractive forces. (Farrokhpay, 2009)

Additionally, ionic dispersants are commonly used in water-based paints, and during the drying paint' stage, the ionised state of this kind of dispersant cannot be maintained. That happens because the water evaporation causes a loss of polarity in the system. This will lead to a loss of stability that will affect optical properties, due to the pigment-particle aggregation. (Farrokhpay, Morris, Fornasiero, & Self, 2010) On other hand, polymeric dispersants will promote a better pigment dispersion and stabilisation which can inhibit the pigment aggregation during the drying stage of the paints. So, for both wet and dry states, polymeric dispersants with both ionic and non-ionic functional groups may have a better  $\text{TiO}_2$  pigment dispersion efficiency. (Farrokhpay, 2009)

The purpose of this thesis was the optimization of  $\text{TiO}_2$  dispersion using polymeric dispersants, to be subsequently used in paints. Their performance was compared with the commercial product, Additol VXW 6200, an acrylic based polymer commonly employed in industrial formulation that was used as a reference.

## 1. Introduction

Synthesis of block copolymers with controlled structure and different molecular weight required in this work has been made by Atom Transfer Radical Polymerization (ATRP) technique. ATRP is a simple and efficient method in which end-functionalization is simple, block copolymerization can be achieved with control over polymer molecular weight and their distribution.

The block copolymers synthesized are hydrophilic and thus soluble in water. It is expected a strong adsorption onto the pigment surface due to the Lewis acid-base interactions between the amine group and the aluminium cations provided by the surface coating treatment of the particles, in order to optimise the pigment application performance. Also, is expected an adsorption by hydrogen bonding between the copolymer synthesized and the surface treatment. Nevertheless, for cationic polyelectrolytes the interaction occurs via electrostatic forces.

A strong adsorption is crucial for an efficient dispersion of the pigment particles. The adsorption process will affect the dispersion quality, which is critical, and the dispersion degree of the pigment particles, which is the main factor in the quality and stability of the paint products, bringing visual and economic benefits. A better dispersion of the particles will require less pigment quantity maintaining the visual properties. Therefore, as  $\text{TiO}_2$  is one of the most expensive raw materials in paint formulations, if this pigment is well dispersed in the paint formulation it will bring economic benefits already mentioned.

## 2. State of the art

### 2.1 Paints and coatings

Paints and coatings play an indispensable role in modern society for aesthetic reasons and as protective agents. Houses, cars, airplanes, computers and other indispensable items are painted and/or coated.

Coating refer to any material applied to a surface, while paint indicates a pigmented material. Paints and coatings are liquid, paste or powder products applied by different methods and equipment, to surfaces, forming an adherent film on the surface of the substrate. (Stoye & Freitag, 1998)

Paints are used to coat and protect a substrate against external agents, and besides that, they give colour and texture to the substrate. To do this, the paints consist in a formulation with a continuous and a discontinuous phase, and their composition is listed in Table 1, as well as the basic function of each component.

**Table 1.** Composition of paints. Adapted from (Lambourne & Strivens, 1999)

	Component	Function
Continuous phase	Solvent	The mean by which the paint may be applied, volatile under specified drying conditions and in which the <i>binder</i> is soluble
	Polymer or resin (binder)	Provides the basis for a continuous film, protecting the surface to which the paint is applied
Discontinuous phase	Additives	Minor components e.g. catalysts and driers.
	Pigments (organic or inorganic)	Provides visual effects.
	Extender	Used for a wide range of purposes including opacity.

The formulation of a paint does not require the use of all components. Depending on the purpose of the application, the major difference occurs in the binder used. (Lambourne & Strivens, 1999)

The most important properties of a paint include: durability, chemical resistance, corrosion resistance, tint strength, uniform colour distribution, easy application, opacity, gloss, and storage stability.

An effective pigment dispersion has a strong influence in the end-use properties required for a paint, like gloss, opacity or colour distribution. (Farrokhpay, 2009)

## 2.2 Pigments

Pigment is a material consisting of organic or inorganic small particles, coloured or fluorescent, practically insoluble in the applied medium, which is used due to their colouring, protective or magnetic properties. One characteristic that distinguishes pigments from soluble organic dyes is their low solubility in solvents and binders. Pigments can be characterized by their chemical composition, and by their optical or technical properties. (Buxbaum & Pfaff, 2005; Herbst & Hunger, 2004)

This definition focuses on aesthetic properties like colour or opacity, and the main use of this material. Pigments can also be used for specific purposes, being known as “extenders”, affecting specific properties such as reinforcement, gloss, hardness or rheological properties. Furthermore, there are pigments that may affect the appearance of the film, but are mainly used to provide different properties like fire retardance, corrosion protection or improve the weatherability of the substrate, by absorbing ultraviolet light and other harmful radiation. (Lambourne & Strivens, 1999)

The pigment colour depends primarily on its chemical structure. The hue (i.e. its colour) of a material is determined by the selective absorption and reflection of incident electromagnetic radiation in ultraviolet and visible regions of the spectrum. (Herbst & Hunger, 2004; Lambourne & Strivens, 1999). Black pigments absorb almost all the light falling upon them, whereas white pigments scatter and reflect virtually all the visible light falling on their surfaces. (Lambourne & Strivens, 1999) A pigment owes its colour due to a combination of the way that scatters and absorbs the incident light. (Hunger, 1999)

Moreover, particle size and crystal structure defines the colour of the pigment. The colour and properties like brightness, shade, purity or colour depth are determined not only by its chemical constitution but also by its physical form. Thus, physical phenomena like light scattering and absorption depends on the size of the particles. (Hunger, 1999) Smaller particles are usually brighter in shade and change the hue of a pigment. (Lambourne & Strivens, 1999) At a particle size of 200-500 nm, organic pigments show their optimum colour properties. Chemically identical substances existing with different crystal structures, property known as polymorphism, can have different colours and physical properties. (Hunger, 1999)

The opacity of a pigment is related to its hiding power. This property is the ability of a pigmented coating to completely cover a surface. It can be defined as the area over which a certain amount of pigmented paint can be spread without losing its opacity. It is dependent of the ability of the film to absorb and scatter light, besides to be also dependent of the film thickness and the pigment's concentration. Colour is also important, dark or saturated colours absorb almost all light falling upon them, covering the surface, whereas yellows do not. At the other extreme,  $\text{TiO}_2$  scatters all the light ensuring that at high enough concentration it will cover the substrate being coated. (Herbst & Hunger, 2004; Lambourne & Strivens, 1999)

The opacifying effect is proportional to the difference between the refractive index (RI) of the pigment and the RI of the medium in which it is dispersed. Both anatase and rutile crystal forms of  $\text{TiO}_2$  have outstanding refractive indices, 2.80 and 2.55, respectively. Indeed, the RI of rutile is the highest of all known white pigments, providing greatest refractive light



scattering, and therefore, the highest opacity. This is one of the main reasons why TiO<sub>2</sub> is universally used as one of the white pigments in paints. (Buxbaum & Pfaff, 2005; Farrokhpay, 2009; Lambourne & Strivens, 1999)

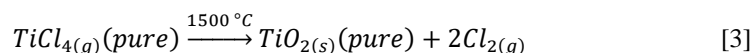
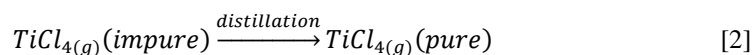
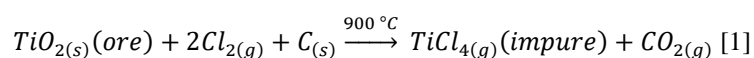
## 2.2.1 Titanium dioxide (TiO<sub>2</sub>)

Titania is the most important white pigment currently consumed in the world, used widely in paint, papermaking, plastic, cosmetic and pharmaceutical industries, due to its outstanding physicochemical properties, like its scattering properties, chemical stability and lack of toxicity. (Buxbaum & Pfaff, 2005; Farrokhpay, 2009)

TiO<sub>2</sub> occurs in a number of crystalline forms. Rutile and anatase are the most important of them, being produced industrially in large quantities. (Buxbaum & Pfaff, 2005; Farrokhpay, 2009) The anatase crystal form is a slighter bluer white and has a softer texture. However, it has two disadvantages, a lower RI (2.55), and is more likely to chalk than the rutile crystal form. Therefore, for surface coatings, the rutile grade is usually preferred. (Lambourne & Strivens, 1999)

Titania is derived from ilmenite or leucosene ores. Depending on economic and environmental factors, titania pigment is produced using the sulphate or the chloride process. The sulphate process is used to produce TiO<sub>2</sub> in the anatase crystal form. In this process, the titanium raw material, which must be soluble in the acid and includes ilmenite and TiO<sub>2</sub> slags, is dissolved in sulphuric acid. Titanium oxyhydrate, washed free of impurities, calcined and surface treated is then precipitated from the resulting solution. (Farrokhpay, 2009)

In the chloride process, the titanium raw material is converted to titanium tetrachloride in a reducing atmosphere. It involves the reaction of chlorine with synthetic rutile to form volatile titanium tetrachloride. After purification and additional fractional distillation, the pure titanium tetrachloride is reacted with oxygen at high temperature in order to produce titania. The unreacted chlorine is recycled to the process. (Farrokhpay, 2009) The chemical reactions are summarized in equations [1] to [3]



In the third step of the reaction, aluminium trichloride (AlCl<sub>3</sub>) is added to TiO<sub>2</sub> to increase the conversion rate of anatase to the rutile form during the base pigment formation, to reduce the pigment aggregation, regulate the crystal growth, enhance photochemical stability by introducing defects into the rutile lattice, which act as traps for photogenerated charges with TiO<sub>2</sub>, and to improve pigment dispersability. The presence of aluminium on the surface is very important for a better dispersion, because alumina has a lower Hamaker constant than titania ( $2.75 \times 10^{-20}$  J and  $6.00 \times 10^{-20}$  J, respectively), decreasing the effect of the Van der Waals attractive forces. (Farrokhpay, 2009)

## 2. State of the art

Rheological properties such as dispersion, aggregation, and surface composition of titania pigment, controls the electrochemical properties, including zeta potential and isoelectric point (iep). (Farrokhpay, 2009)

Another advantage of TiO<sub>2</sub> is the ability to prepare pigment particles with an optimum crystal and particle size, necessary to obtain the maximum scattering of visible light due to a relatively narrow size distribution. A high RI combined with the optimum particle size is the main reason for the excellent hiding power of titania pigment. (Farrokhpay, 2009)

Polymeric dispersants are added to pigment suspensions to improve dispersion properties. Despite inorganic coatings are applied to the titania pigment surface to improve pigment dispersion, in practical applications this is not always sufficient to fully stabilise the pigment particles. (Farrokhpay, 2009)

### 2.3 Particles stabilization

Dispersion stabilization in aqueous dispersions is provided by two major mechanisms, electrostatic and steric stabilization.

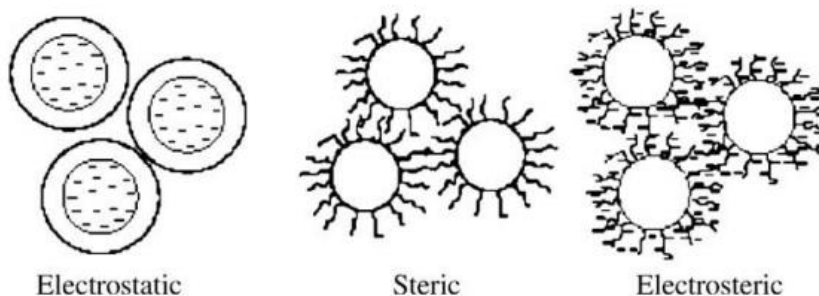
In an aqueous system, electrostatic stabilization involves adsorbed ions building up a charged layer around the pigment, preventing aggregation by electrostatic repulsion. Anionic polymers are well known to provide electrostatic stabilization. However, the stabilizing charge can be quickly reduced by the presence of external agents, like with the addition of other pigments with different surface charge properties or with surface or ionic solution impurities. (Farrokhpay, Morris, Fornasiero, & Self, 2005; Farrokhpay, 2009)

Steric stabilization comprehends polymer adsorption to the particle surface at a minimum of one point, and is generally described to derive from two factors: a volume restriction component due to crowding, because the interacting species begin to lose certain degrees of freedom, and a mixing or osmotic component, involving compression of the adsorbed layer causing an increase in polymer concentration. (Myers, 1999)

Ionic polymeric dispersants stabilize the pigment particles via electrostatic and steric forces, requiring small concentrations. However, these dispersants are sensitive to pH, ionic strength and to the presence of multivalent ions. On the other hand, non-ionic polymeric dispersants provide only steric stabilization and have the advantage of being pH insensitive, but they must be used in higher concentrations. (Farrokhpay, 2009)

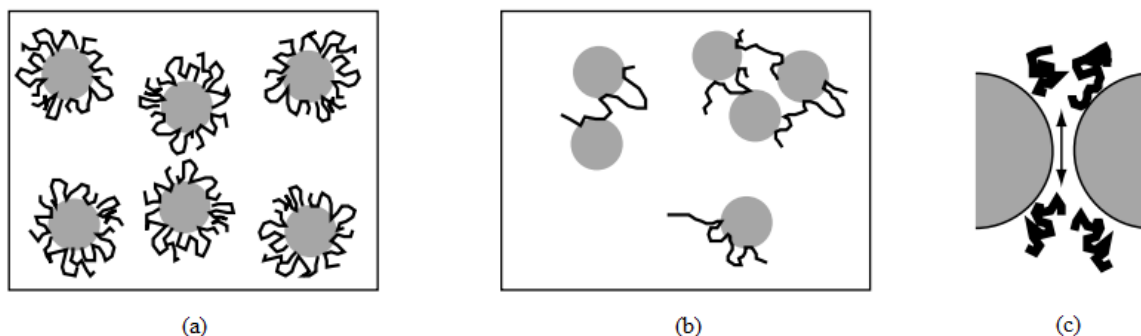
It is also possible to combine both mechanisms to stabilize pigment particles, creating a stabilization mechanism known as electrosteric stabilization. (Farrokhpay, 2009) Amphiphilic block copolymers can be used as dispersants for aqueous suspensions stabilization due to its selective anchoring characteristic, that may link the hydrophobic block to the pigment surface, while the hydrophilic block promotes electrosteric stabilization. (Creutz & Jérôme, 1999; Monteiro et al., 2014) However, cationic polyelectrolytes will adsorb onto the pigment surface

via attractive electrostatic interactions between oppositely charged ions. A schematic diagram of all the mechanisms of stabilization is shown in Figure 1. (Farrokhpay, 2009)



**Figure 1.** Stabilization mechanisms in particle suspensions. (Farrokhpay, 2009)

The polymer concentration and molecular weight are two important factors in order to have a stabilized dispersion. In systems containing a low polymer concentration and/or very high-molecular-weight polymer, molecules can become adsorbed to more than one particle leading to “bridging” flocculation, while in stabilized systems an adsorbed polymer molecule will be associated with one particle. Another phenomenon, termed depletion flocculation, may occur if the polymer is not adsorbed or poorly adsorbed. In depletion flocculation, the polymer chains that are weakly adsorbed or not adsorbed at all, are rejected of the area, displacing the osmotic balance. As a consequence, there will be a loss of stability and posterior flocculation. (Myers, 1999)



**Figure 2.** Stabilized system (a). “Bridging” flocculation (b) Depletion flocculation (c). Adapted from (Myers, 1999)

## 2.4 Polymeric Dispersants

Polymeric pigment dispersants are an important tool to make optimum use of pigments and to optimize the performance of paints. (Auschra, Eckstein, Mühlebach, Zink, & Rime, 2002) A suitable dispersant will improve the end-use properties like gloss, opacity, tint strength, colour distribution or storage stability, and will reduce the fabrication costs of the paint. Polyacrylic acid and polyacrylamide are broadly used in industry as dispersants. The most

## 2. State of the art

reasonable stabilisation mechanism of TiO<sub>2</sub> pigments with these dispersants is through electrostatic interactions. (Farrokhpay et al., 2005, 2010)

Polymeric pigment dispersants contain soluble polymeric chains and segments with affinity to the pigment (anchoring groups). (Auschra et al., 2002) In order to have a polymeric dispersant adsorbed on the pigment surface, anchoring groups need to be able to adsorb strongly onto the particle. Amines, ammonium and quaternary ammonium groups, carboxylic, sulphonic and phosphoric acid groups and their salts, acid sulphate and phosphate ester groups are examples of functional groups that can be used to anchor polymeric chains to mineral oxide particles. (Farrokhpay, 2009)

The molecular weight of polymeric dispersants is stated to be less than 20 000 g/mol, but it must be enough to provide to the polymer chains, an optimum length to overcome the Van der Waals forces of attraction between pigment particles. (Farrokhpay, 2009)

There is a need to improve dispersants efficiency in aqueous dispersions which can reduce the process costs, given that TiO<sub>2</sub> is an expensive pigment, and a better dispersion of it can reduce the amount of pigment used in a paint formulation.

Amphiphilic block copolymers are a suggested alternative to the dispersants used industrially in order to improve TiO<sub>2</sub> pigment dispersion and stability.

Creutz and Jérôme (1999) reported the use of diblock copolymers of 4-vinylpyridine (4VP) or 2-vinylpyridine (2VP) and sodium methacrylate (MANa) as dispersants for aqueous solutions of TiO<sub>2</sub> coated with alumina. P4VP and P2VP blocks have proved to be strong anchoring blocks for TiO<sub>2</sub>. The polyelectrolyte block forms an electrosteric barrier against coalescence and no depletion flocculation occurred. (Creutz & Jérôme, 1999)

In 2000 the same authors studied another diblock copolymer of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and MANa with the same purpose. PDMAEMA block is anchored onto the TiO<sub>2</sub> surface coated with alumina as strongly as the adsorption enthalpy of the hydrophobic block is high. The polyelectrolyte is an electrosteric barrier against flocculation and can efficiently disperse TiO<sub>2</sub> aqueous solutions. (Creutz & Jérôme, 2000)

Amine-type pendent groups, such as 4VP or DMAEMA, are expected to adsorb onto alumina by hydrogen bonding with the surface hydroxyl groups, and by Lewis acid–base interactions with aluminium cations as well. (Creutz & Jérôme, 1999, 2000)

More recently, Karakaş and Çelik (2013) studied the effect of sodium polyacrylate (NaPAA) on the stability of TiO<sub>2</sub> suspensions coated with zirconia and alumina. This polymer is used widely as a dispersant in paint formulations and PAA-based dispersants are generally used to accomplish the electrosteric repulsion. A proper dispersion and stability of TiO<sub>2</sub> particles will depend in the suspension pH, polymer concentration and adsorption density of NaPAA used as a dispersant. (Karakaş & Çelik, 2013)

Monteiro and co-authors (2014) reported the dispersion and stabilization of TiO<sub>2</sub> nanoparticles in water using amphiphilic block copolymers of poly(ethylene glycol)-block-poly(4-vinyl pyridine) (mPEG-b-P4VP) as a dispersant. Well-defined copolymer blocks of different molecular weights were prepared, apparently yielding more agglomerated particle size distribution in water than NaPAA, but having a better performance in terms of dispersion stability along time. (Monteiro et al., 2014)

## 2.5 Reversible-deactivation radical polymerization (RDRP)

Copolymer synthesis can be made by two main different polymerization mechanisms such as step-growth polymerization and chain-growth polymerization.

Summarily, chain-growth polymerization involves the sequential addition of unsaturated molecules to a rapidly growing chain, and is induced by the addition of free-radical-forming reagents or by ionic initiators (cationic or anionic). It involves three fundamental steps: initiation, propagation, and termination. A fourth step, chain transfer, may be involved as well. (Ebewele, 2000; Kumar & Gupta, 2003) Ionic polymerization technique is demanding, requiring high-purity starting reagents, and the use of high-vacuum procedures to prevent unexpected termination due to the presence of impurities, to prepare well-defined block copolymers. (Hamley, 2004)

The step-growth polymerization occurs between pairs of chemically reactive or functional groups on the reacting molecules. The reaction occurs between any two species at any time, leading to a larger molecule with a steady raise of polymer molecular weight. Step-growth polymerizations can be divided into two main groups: polyaddition, in which monomers react without the elimination of any small molecule, and polycondensation, in which a small molecule is eliminated at each step. (Ebewele, 2000)

Furthermore, chain-growth polymerization do not allow to control the molecular weight and the molecular weight distribution due to the very short lifetime of the growing chains, which is a consequence of chain-terminating steps. The short lifetime of the growing chains also means that is impossible any synthetic manipulation, end functionalization or addition of a second monomer to make a block copolymer. (Braunecker & Matyjaszewski, 2007) In step-growth polymerization, the monomer is quickly consumed, since any two monomers can react at any time providing only control over the polymer molecular weight. Due to the target of produce controlled block copolymers, both techniques described early are not suitable choices to synthesize uniform macromolecules.

New advanced materials targeting specific applications requires the synthesis of uniform macromolecules with precisely controlled size, novel topology, composition, and functionality. (Matyjaszewski, 2012) The Reversible Deactivation Radical Polymerizations (RDRP) are an approach to gain control over the chain growth, satisfying the ultimate goal of tuning the polymer properties at the molecular level, because all chains are instantaneously initiated and grow concurrently without significant occurrence of chain breaking reactions, like termination or/and transfer. (Matyjaszewski, 2012; Qiu, Charleux, & Matyjaszewski, 2001)

The most widely used RDRP methods are atom transfer radical polymerization (ATRP), stable free radical polymerization, most often nitroxide-mediated (NMP), and degenerative transfer polymerization such as reversible addition-fragmentation chain transfer (RAFT) polymerization. RDRP techniques make possible to create polymers with narrow molecular weight distributions (MWDs) and controlled molecular weights (MWs), architecture, composition, topology or functionality. (Matyjaszewski & Tsarevsky, 2009)

Common features of controlled radical polymerization are internal first-order kinetics with respect to monomer (due to negligible termination and fast initiation, the logarithmic

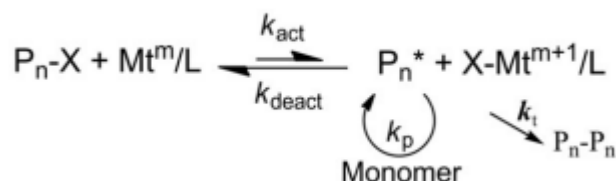
## 2. State of the art

monomer concentration is a linear function with time), linear growth of degree of polymerization (DP) with conversion, narrow molar mass distribution, and long-lived polymer chains. (Qiu et al., 2001)

Among the different RDRP methods, ATRP presents several key advantages for the synthesis of the block copolymers envisaged in this work: simple protocols, mild reaction conditions and tolerance to several monomer functionalities.

### 2.5.1 Atom Transfer Radical Polymerization (ATRP)

ATRP is based on the transition-metal complexes mediated fast equilibrium between dormant and active species. Alkyl (pseudo)halide initiators or dormant macromolecular species (RX/P<sub>n</sub>X) react with transition-metal complexes in their low-oxidation state Mt<sup>m</sup>/L acting as activators, (Mt<sup>m</sup> represents the transition-metal species in oxidation state m, and L is a ligand), to reversibly form propagating radicals (P<sub>n</sub><sup>\*</sup>) and deactivators (transition-metal complexes in the higher-oxidation state coordinated with (pseudo)halide ligands X-Mt<sup>m+1</sup>/L). The generated macroradical (P<sub>n</sub><sup>\*</sup>) reacts with higher oxidation state transition metal complex forming dormant species and regenerating the activator. The dormant species in this ATRP equilibrium can be polymer chains able to grow in one or many directions. (Matyjaszewski & Tsarevsky, 2009; Matyjaszewski, 2012; Mendonça, Serra, Coelho, Popov, & Guliashvili, 2011)



**Figure 3.** ATRP equilibrium. (Matyjaszewski, 2012)

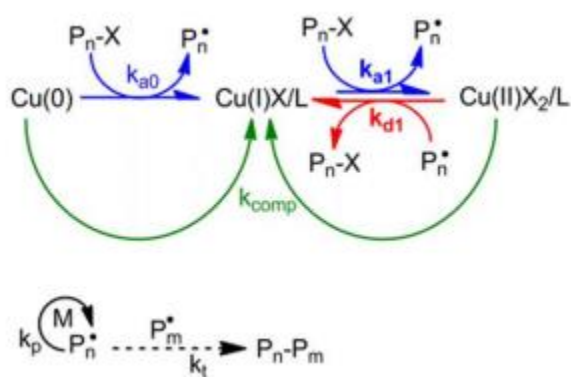
ATRP is a catalytic process and has been successfully mediated by a variety of metals, including Ti, Mo, Re, Fe, Ru, Os, Rh, Co, Ni, Pd and Cu. Complexes of Cu are the most efficient catalysts in the ATRP for a broad range of monomers in diverse mediums. (Braunecker & Matyjaszewski, 2007; Matyjaszewski, 2012)

Control over polymer molecular weight is due to 5 factors: rate of initiation is at least comparable with the rate of propagation, allowing simultaneous growth of all polymer chains; the exchange between species of different reactivities is faster than propagation, ensuring all active chains terminated are equally susceptible to reaction with monomer for a uniform growth; chain transfer or termination can be neglected; rate of depropagation is considerably lower than propagation. This guarantees that the polymerization is irreversible; and system is homogeneous, and the mixing is sufficiently fast. (Qiu et al., 2001)

ATRP have numerous advantages such as: initiators are commercially available; end-functionalization is quite simple; block copolymerization can be achieved in any order and a large range of temperatures can be employed beyond those already referenced; broad range of monomers polymerized by this technique. (Braunecker & Matyjaszewski, 2007)

Usually, high amounts of metal catalyst are required in normal ATRP reactions. However, ATRP does not depend on the absolute catalyst concentration, but on the ratio of activator and deactivator concentrations. Consequently, new ATRP techniques have been developed to operate at extremely low catalyst concentrations.

One of these methods is the supplemental activator and reducing agent (SARA) ATRP, which uses zerovalent transition metals as both reducing agents and supplemental activators. When Cu(0) is used in the reaction, it slowly regenerates Cu(I)X species *in situ* as a reducing agent, and it slowly generates radical and Cu(I)X by a supplemental activator. Furthermore, due to the high activity of Cu(I) in activating alkyl halides, its concentration is at so low levels that disproportionation occurs at a very slow rate and can be neglected during polymerization. In this system, the majority of alkyl halide activation events and deactivations of growing radicals are ruled by the ATRP equilibrium. (Mendonça et al., 2014)



**Figure 4.** General mechanism of SARA ATRP mediated by Cu(0) and Cu(II)X<sub>2</sub>. (Mendonça et al., 2014)

For many applications, the removal of the small amount of catalyst is unnecessary. (Matyjaszewski & Tsarevsky, 2009)

Between the different architectures that a polymer can exhibit, block copolymers fit well to act as pigment dispersants. (Auschra et al., 2002)

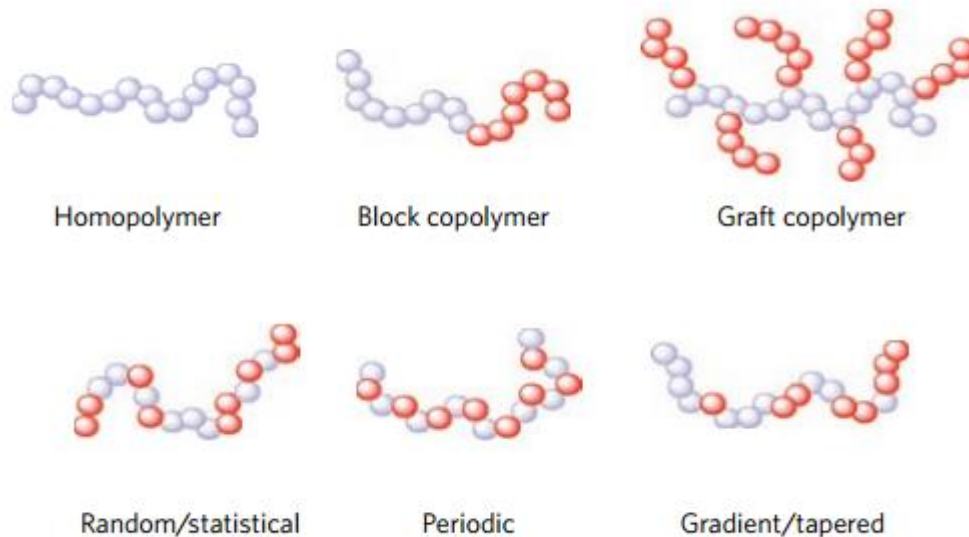
## 2.6 Block copolymers

Polymers are materials of very high molecular weight with numerous applications in our modern society, whether as natural polymers such as cellulose, silk, wool and cotton, or synthetic polymers like polyethylene, polystyrene or polypropylene. They are obtained through the chemical reactions of small molecular compounds called monomers, the repeating unit, bound together by covalent bonds. (Kumar & Gupta, 2003)

The number of repeating units is known as the degree of polymerization (DP), and it represents one way of quantifying the molecular length or size of a polymer. Molecular weight is another way to quantify it and by definition,  $M_n = DP \times M_0$  (Ebewele, 2000)

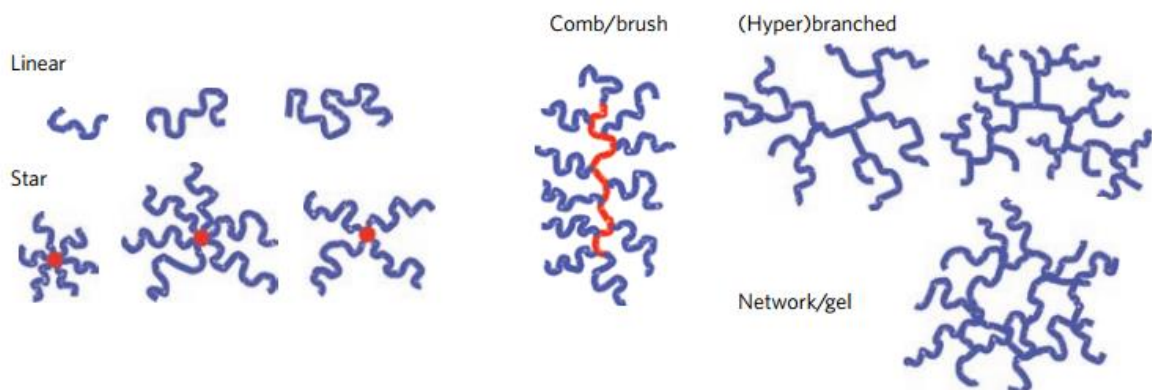
## 2. State of the art

Polymers with only one repeating unit are known as homopolymers. However, the polymer chain can have more than one repeating units, being defined as copolymers. This repeating units may be arranged in various degrees of order along the backbone. (Ebewele, 2000) The composition of the polymer or the way that the repeating units are organized in the backbone lead to different designations (Figure 5).



**Figure 5.** Schematic representation of polymer system. Adapted from (Matyjaszewski & Tsarevsky, 2009)

Polymers can also exhibit different topologies, as represented in Figure 6.

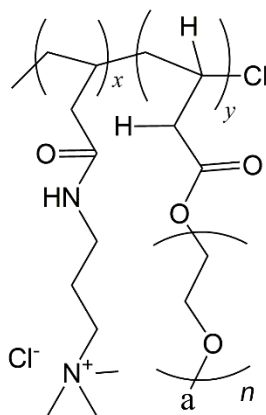


**Figure 6.** Schematic representation of polymer architecture. Adapted from (Matyjaszewski & Tsarevsky, 2009)

When a hydrogen atom is bonded to a strongly electronegative atom, such as N, the hydrogen atom is able to accept electrons from -OH groups of the hydrated surface of alumina, resulting in the formation of hydrogen bond. (Farrokhpay, 2009) AMPTMA ((3-acrylamidopropyl)trimethylammonium chloride) is an amine and, like 4VP or DMAEMA, is expected to adsorb onto alumina by hydrogen bonding with the surface hydroxyl groups, and by Lewis acid–base interactions with aluminium cations as well. (Creutz & Jérôme, 1999, 2000)



In a solvent, block copolymer phase behaviour is controlled by the interaction between the segments of the polymers and the solvent molecules as well as the interaction between the segments of the two blocks. (Hamley, 2004)



**Figure 7.** P(AMPTMA)-*b*-P(OEOA) chemical structure

In order to be an efficient pigment dispersant, P(AMPTMA)-*b*-P(OEOA) must be strongly adsorbed onto the pigment surface. This adsorption occurs due to the hydrogen bonding between the nitrogen atom of AMPTMA and -OH groups of the hydrated surface of alumina, leading to the formation of a barrier around TiO<sub>2</sub> particles preventing aggregation, and also due to the Lewis acid-base interactions.

However, as Creutz & Jérôme reported, the Lewis acid-base interactions between the amine group, a typical Lewis base, and aluminium cations should also contribute to the amine anchoring onto alumina-coated TiO<sub>2</sub>. (Creutz & Jérôme, 1999)

As AMPTMA is a cationic polyelectrolyte, the adsorption must occur via electrostatic interactions.

### 2.6.1 Copolymers characterization

Polymers can be monodispersed, with a single molecular weight, or polydisperse, and have a molecular weight distribution. In most cases, a mixture of molecules with different degrees of polymerization is obtained. (Teraoka, 2002) For the vast majority of polymers, a tighter molecular distribution leads to better properties. (Sperling, 2005)

Control over the polymerization must be proved after the synthesis. To accomplishing that, copolymers must be characterized in order to determine their molecular weight ( $M_n$ ) and dispersity ( $\mathcal{D}$ ).

Number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and dispersity index ( $\mathcal{D}$ ) are defined in equations, 4, 5 and 6, respectively, where  $n_i$  is the number of chains with exact molecular weight  $M_i$ .

$$M_n = \sum_i \frac{n_i M_i}{\sum_i n_i} \quad [4]$$

$$M_w = \sum_i \frac{n_i M_i^2}{\sum_i (n_i M_i)} \quad [5]$$

$$\mathcal{D} = M_n / M_w \quad [6]$$

Number-average molecular weight ( $M_n$ ) can also be determined by Hydrogen-1 Nuclear Magnetic Resonance ( $^1\text{H}$  NMR) as well as polymer conversion.

$$M_n^{th} = DP \times conversion + M_{\text{initiator}} \quad [7]$$

Copolymers characterization must prove common features of RDRP techniques like narrow molar mass distribution, which is proved by the  $\mathcal{D}$  that ideally should be less than 1.1. Another feature proved in the characterization is the livingness of the polymer chains, that is a consequence of the residual termination and chain transfer during the polymerization, allowing the preparation of block copolymers. (Qiu et al., 2001)

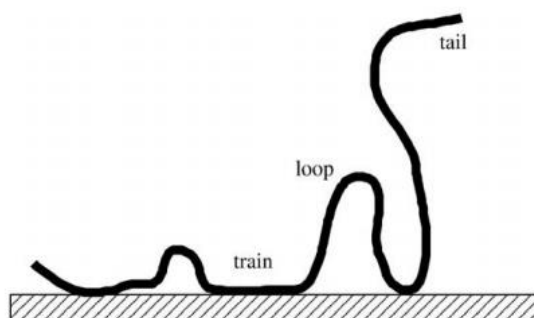
Reaction can be confirmed by the movement of polymer molecular weight in SEC chromatography and by  $^1\text{H}$  NMR to confirm the structure of the copolymer by comparison of the characteristic signals with those reported in literature.

## 2.7 Adsorbed polymer conformation

Polymer adsorption mechanism and conformation depends on the type of interaction between the polymer and the pigment surface. In charged surfaces like titanium dioxide coated with alumina, the adsorption involves the interaction between charges, the polymer capability to adsorb onto the surface through electrostatic interactions and is highly dependent on the experimental conditions, the nature of the surface and ionic strength. (Myers, 1999)

Conformation of the adsorbed polymer is a major controlling factor in determining the stability or dispersion of the mineral suspensions. Steric stabilizers must be strongly anchored in one point or more efficiently in several points. A polymer may be adsorbed at one end of the chain, single point attachment to produce tails, or in loops and tails for multiple points attachment. Trains are the segments connected to the surface. Variation in length of the trains, loops and tails, controls the adsorbed conformation and the adsorbed layer thickness. (Farrokhpay, 2009; Myers, 1999)

According to Myers, a system with loops will only produce a thicker adsorbed layer for a given polymer chain length, but a system with loops and trains will result in a stronger adsorption and a higher chain density. (Myers, 1999)



**Figure 8.** Schematic representation of adsorbed polymer molecule at the solid–liquid interface. (Farrokhpay, 2009)

Polymeric dispersant adsorption onto mineral oxides is influenced by many variables including surface molecular architecture, dispersant structure, chemical functional groups types, and the solvent displacing ability of polymer segments. (Farrokhpay, 2009)

Polymer functional groups activity and type, influence the polymer solution chemistry. For anionic polymers, the solution pH and ionic strength influence the polymer conformation in solution, because both variables determine the degree of dissociation of the anionic functional groups. For example, at pH values where no dissociation occurs, the polymer behaves as a non-ionic polymer adsorbing in extended layer with relatively short loops and long dangling tails. (Farrokhpay, 2009)

The conformation of an ionic polymer depends on the ionic strength of the solution. At low ionic strength the polymers adsorb in thin layers and has an extended conformation due to the electrostatic repulsion energy between charged groups being stronger than the conformational energy. Instead, at high ionic strength, the adsorbed layer thickness increases due to the occurrence of loops and tails because the electrostatic repulsion is reduced. (Farrokhpay, 2009)

Another important variable in the adsorption process is polymer  $\bar{M}$ . A polydisperse polymer will adsorb high molecular weight species rather than the lower molecular species. Also, charge and charge density of both the adsorbate and the metal oxide surface strongly influence the adsorption of ionic dispersants onto metal oxides. Adsorption is generally not favoured when both of them have the same charge. (Farrokhpay, 2009)

The polymer adsorption onto the oxide surface is favoured with the increase of the polymer molecular weight. (Farrokhpay, 2009) The conformations originated by the polymers when adsorbed onto the surface are expected to provide an effective barrier against flocculation.

The main goal of this work is stabilize  $\text{TiO}_2$  particles with a cationic block copolymer, and all the copolymers synthesized are on the 20 000 g/mol edge or slightly above this molecular weight reference, for the copolymers acting as pigment dispersants. The cationic polyelectrolyte block will promote hydrogen bonding, Lewis acid-base interactions to the coated surface of the pigment, but mostly via electrostatic interactions of the cationic group to strongly anchor onto the pigment surface ensuring the particle stabilization. The OEOA block is expected to provide efficient steric stabilization preventing pigment agglomeration. So, for PAMPTMA-*b*-POEOA copolymer the stabilization mechanism will be mainly based on both electrostatic and steric interactions.



### 3. Experimental

#### 3.1 Materials

The TiO<sub>2</sub> sample used during this study was mostly composed by TiO<sub>2</sub> rutile crystal form in a minimum content of 93% with Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and other organic compounds on the surface. This sample has the commercial name of KEMIRA and is a typical commercial pigment used in the paint industry. The particles have a refractive index of 2.7, a mean crystal size around 220 nm and pH between 7.6 and 8.6. The commercial polymeric dispersant Additol VXW 6200 has been used as a reference to evaluate the novel block copolymers efficiency as dispersants. Both titania pigment sample and Additol VXW 6200 have been kindly supplied by Resiquímica.

(3-acrylamidopropyl)trimethylammonium chloride (AMPTMA) (solution 75wt. % in H<sub>2</sub>O, Aldrich), ethyl 2-chloropropionate (ECP) (99%, Aldrich), deuterium oxide (D<sub>2</sub>O) (+99%; Sigma-Aldrich), copper(II) chloride (CuCl<sub>2</sub>) (+99% extra pure, anhydrous; Acros) and methanol (MeOH) (>99,85%, Sigma-Aldrich) were used as received.

Poly(ethylene glycol) methyl ether (OEOA) (99%, Mw=480 Da, Aldrich) was passed over a column filled with basic alumina and sand to remove inhibitor prior to use. Copper (0) wire (99%; Acros) was activated in a solution (HCl/MeOH = 30/70 (v/v)) rinsed with methanol and dried before use. Milli-Q water (MilliQ®, Millipore) was obtained by reverse osmosis.

Tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>TREN) was synthesized as reported in the literature. (Britovsek, England, & White, 2006)

#### 3.2 Synthesis

##### 3.2.1 PAMPTMA

SARA ATRP of AMPTMA followed a reported method (Mendonça et al., 2014) using Cu(0) wire and [CuCl<sub>2</sub>]/[Me<sub>6</sub>TREN]=1/1 catalytic system in an eco-friendly solvent mixture EtOH/H<sub>2</sub>O (1:1) followed the subsequent procedure: AMPTMA (1.4 mL, 5.4 mmol), a solution of CuCl<sub>2</sub> (6.1 mg, 45 μmol) and Me<sub>6</sub>TREN (20.9 mg, 91 μmol) in water (1.4 mL) and a solution of ECP (12.4 mg, 91 μmol) in ethanol (1.9 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stirrer bar, and then, the resultant solution was frozen. After, activated Cu(0) wire (l = 10 cm; d = 1 mm) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with five freeze-vacuum-thaw cycles and purged with nitrogen. The reaction was allowed to proceed with stirring (700 rpm) at 30°C in a water bath. It was scheduled the collection of different reaction mixture samples during the polymerization and analysed by <sup>1</sup>H NMR spectroscopy in order to determine the monomer conversion, and by aqueous SEC to determine the polymer molecular weights and their dispersity.

### 3.2.2 PAMPTMA-*b*-POEOA

PAMPTMA-*b*-POEOA has been synthesized according to a reported method (Mendonça et al., 2014). In a typical “one-pot” chain extension, AMPTMA (3.6 mL, 14.5 mmol), a solution of CuCl<sub>2</sub> (16.3 mg, 121 μmol) and Me<sub>6</sub>TREN (55.7 mg, 242 μmol) in water (5.0 mL) and a solution of ECP (33.0 mg, 242 μmol) in ethanol (3.7 mL) were added to a 50 mL Schlenk flask equipped with a magnetic stirrer bar, and then, the resultant solution was frozen. Next, activated Cu(0) wire (l = 10 cm; d = 1 mm) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with five freeze-vacuum-thaw cycles and purged with nitrogen. The reaction was allowed to proceed with stirring (700 rpm) at 30°C in a water bath. After the desired reaction time, corresponding to the time where the monomer conversion reached more than 80 %, a degassed mixture of OEOA (4.26 mL, 9.7 mmol) previously passed over a basic alumina and sand column, as described early, water (7.1 mL) and ethanol (7.1 mL) were added to the Schlenk flask under nitrogen and the reaction proceeded with the exact same conditions (stirring at 700 rpm at 30°C in a water bath). In the end, a reaction sample has been collected and analysed by <sup>1</sup>H NMR spectroscopy in order to determine the monomer conversion, and by aqueous SEC to determine the polymer molecular weights and their dispersity.

PAMPTMA<sub>52</sub>-*b*-POEOA<sub>39</sub>, PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub>, PAMPTMA<sub>30</sub>-*b*-POEOA<sub>28</sub> has been synthesized following this typical procedure with a monomer concentration of 1.45M, while PAMPTMA<sub>85</sub>-*b*-POEOA<sub>14</sub> has been synthesized with a monomer concentration of 2.45M.

The block copolymer was then dried in two equipment. First, it has been dried in a rotary evaporator to remove the ethanol. Further, it has been dried in a freeze-drier to fully remove the vestigial water that can still be present, which allow to obtain the final copolymer.

## 3.3 Characterization

### 3.3.1 Size Exclusion chromatography (SEC)

Size Exclusion chromatography (SEC) was accomplished using a system equipped with an online degasser, a refractive index (RI) detector and a set of columns: Shodex OHpak SB-G guard column, OHpak SB-804HQ and OHpak SB-804HQ columns. The polymers were eluted using 100 mM sodium phosphate buffer with 0.2 vol % trifluoroacetic acid (pH = 2) at a flow rate of 1.0 mL/min. Before the injection (100 μL), the samples were filtered through a polytetrafluoroethylene (PTFE) membrane with a 0.45 μm pore. The system was calibrated with five narrow poly(ethylene glycol) standards and the molecular weights were determined by conventional calibration using the Clarity software version 2.8.2.648.

Number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and dispersity index ( $D$ ) of block copolymers were characterized by SEC. 4 mg of each sample was weighted, dissolved in Milli-Q water and filtered to SEC analysis.

### 3.3.2 Nuclear Magnetic Resonance ( $^1\text{H-NMR}$ Spectra)

Monomer conversion was determined using  $^1\text{H}$  NMR spectroscopy in  $\text{D}_2\text{O}$ , using a Bruker Avance III 400MHz spectrometer, with a 5-mm TIX triple resonance detection probe with tetramethylsilane (TMS) as an internal standard with spectra analysed using MestRenova software version: 6.0.2-5475. The PAMPTMA homopolymer and PAMPTMA-*b*-POEOA block copolymers has been analysed in  $\text{D}_2\text{O}$ .

For  $^1\text{H}$  NMR analysis, approximately 4 drops from the reaction solution were mixed with 560 $\mu\text{L}$  of  $\text{D}_2\text{O}$ .

### 3.3.3 Dynamic Light Scattering (DLS) and Zeta Potential measurements

Particle size distribution (in intensity), average hydrodynamic particle size average (z-average) and polydispersity index (PDI) were measured using a Malvern Instruments Zetasizer Nano-ZS and determined with Zetasizer software version: 7.11. Dynamic Light Scattering (DLS) measurements were performed at 25°C and at a backward scattering angle of 173°. Zeta potential measurements has been done in the same equipment with a laser Doppler electrophoresis and determined with a Smoluchovski model.

The samples for DLS and zeta potential measurements were prepared according to Rocha and co-authors (Rocha et al., 2014) where 5 mg of each copolymer has been diluted in 1 mL of Milli-Q water at pH 9.5 and left under mechanical stirring for 16 hours. Also, a solution of Milli-Q water with 0.1 mg/mL of  $\text{TiO}_2$  particles has been prepared with ultrasonication to disperse the particles for 2 minutes at 90% amplitude. Just before the first analysis, 5 mL of this solution has been added to the copolymers solution.

For DLS measurements, 1.5 mL of each sample was removed from the suspensions, placed in the quartz cuvette, hand shaken and analysed. For zeta potential measurements 1 mL was taken from the top of the suspension, placed in the capillary cell, and analysed. DLS measurements has been repeated after 3 and 5 days without shaking the samples. Each sample has been measured three times in both DLS and Zeta Potential analysis and the result analysed is the mean of these 3 values.





## 4. Results and Discussion

### 4.1 Block copolymers characterization

The use of an ATRP method to prepare water soluble PAMPTMA-*b*-POEOA copolymers allowed to obtain block copolymers with controlled molecular weight and dispersity. Also, PAMPTMA homopolymers have been synthesized. Table 2 presents the characterization and the reaction time of the different polymers synthesized during this work.

**Table 2.**  $M_n$  determined by SEC and  $^1\text{H NMR}$  and  $M_w/M_n$  determined by SEC for the synthesized polymers.

Block copolymer	target DP	Time (h)	Monomer conversion (%)	$M_n, ^1\text{H NMR}$ (g/mol)	$M_n, \text{GPC}$ (g/mol)	$\bar{D}$ (PDI)
PAMPTMA <sub>32</sub>	35	0.75	91.2	8 602	7 483	1.13
PAMPTMA <sub>54</sub>	60	1	89.2	14 286	16 187	1.12
PAMPTMA <sub>84</sub>	100	1	83.5	22 013	22 092	1.12
PAMPTMA <sub>52</sub>	60	0.67	86.2	10 432	18 066	1.11
PAMPTMA <sub>52-b-POEOA</sub> <sub>39</sub>	40	17.42	92.4	28 178	23 088	1.22
PAMPTMA <sub>38</sub>	45	0.62	84.7	7 977	13 863	1.13
PAMPTMA <sub>38-b-POEOA</sub> <sub>36</sub>	41	16.63	87.9	25 281	23 016	1.19
PAMPTMA <sub>30</sub>	36	0.53	82.7	6 058	11 818	1.14
PAMPTMA <sub>30-b-POEOA</sub> <sub>28</sub>	30	16.37	94.4	19 649	14 536	1.21
PAMPTMA <sub>85</sub>	90	2.1	94.5	17 061	21 774	1.12
PAMPTMA <sub>85-b-POEOA</sub> <sub>14</sub>	15	3.28	96.6	24 013	24 555	1.12

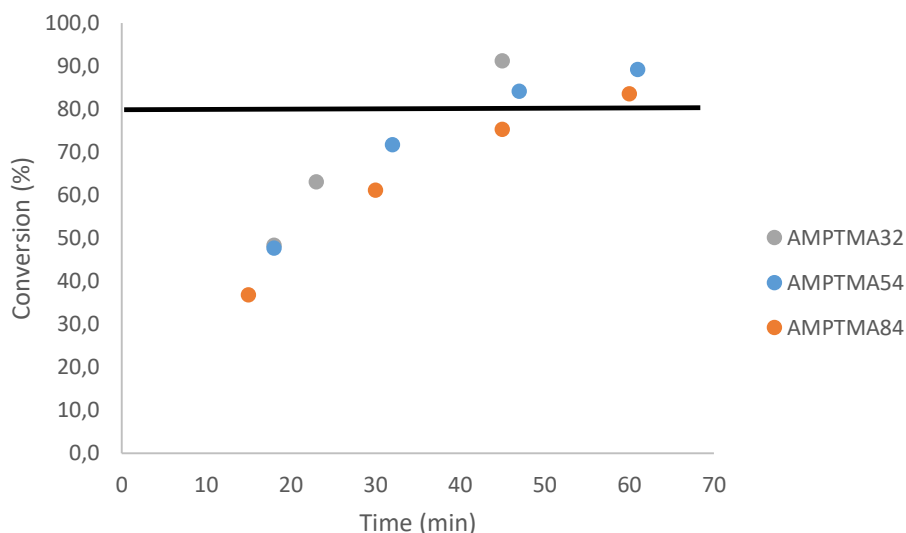
According to Qiu and co-authors (Qiu et al., 2001) a controlled polymerization is expected to produce a polymer with a polydispersity around 1.1. However,  $\bar{D}$  below 1.5 is acceptable as a controlled reaction. All PAMPTMA-*b*-POEOA copolymers synthesized have a polydispersity below 1.22, so the narrow molecular weight distribution is an evidence of the success of each synthesis.

Farrokhpay referred that the preferred molecular weight for polymeric dispersants is less than 20 000 g/mol, but the molecular weight of them must be sufficient to overcome the Van der Waals forces of attraction between pigment particles. If chains are too short, pigment particles will aggregate and cause dispersion instability. In the other hand, too long chains have tendency to fold onto themselves causing flocculation, and a high potential of particle-particle bridging. (Farrokhpay, 2009) Thus, copolymers with different DP's have been synthesized to

#### 4. Results and Discussion

study their pigment dispersion stability. According to SEC analysis, only PAMPTMA<sub>30</sub>-*b*-POEOA<sub>28</sub> have a molecular weight below 20 000 g/mol but the other copolymers have molecular weight near to this value, with a maximum error of 23% for PAMPTMA<sub>85</sub>-*b*-POEOA<sub>14</sub> block copolymer.

A previous study of the SARA ATRP of AMPTMA polymerization has been made in an early phase of this work. This study was carried out to determine the reaction time for the addition of OEOA monomer, which has been considered the 80% conversion of AMPTMA. PAMPTMA<sub>32</sub>, PAMPTMA<sub>54</sub> and PAMPTMA<sub>84</sub> has been synthesized with this purpose.

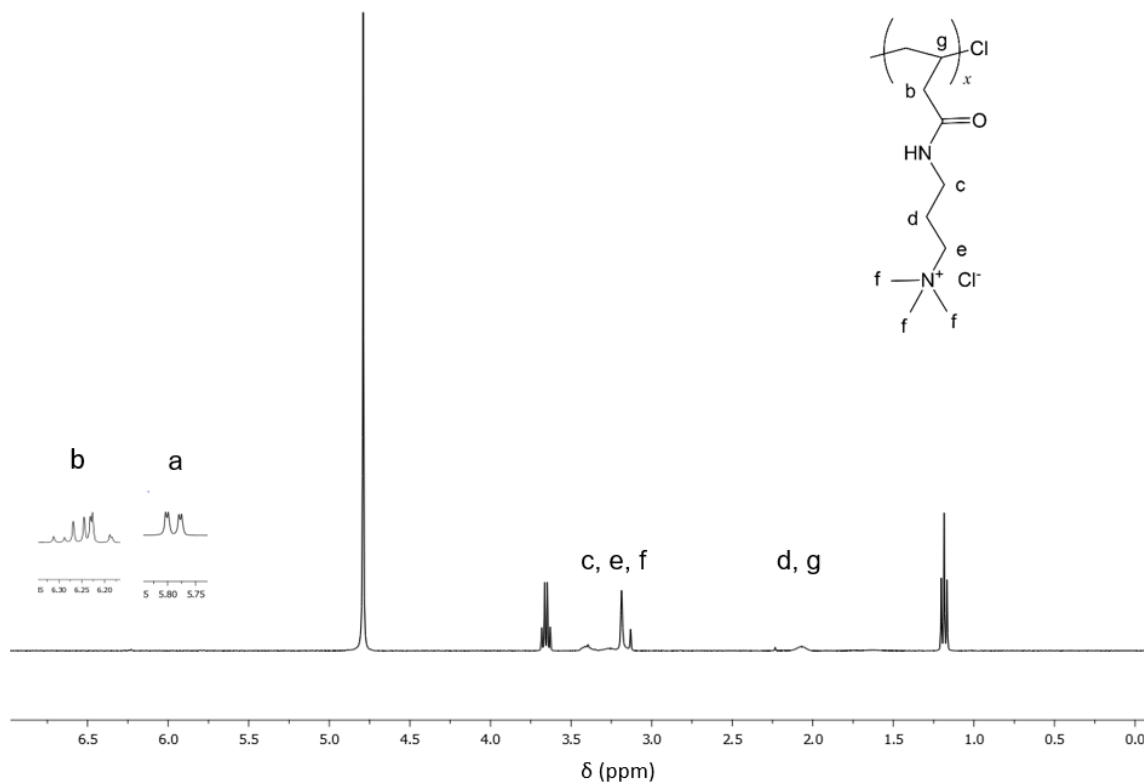


**Figure 9.** Conversion vs. time for the SARA ATRP of AMPTMA

From Figure 9, it is possible to conclude that there is a positive relation between the time needed to reach more than the 80 % AMPTMA monomer conversion goal and the target degree of polymerization. For the target degree of polymerization of 35, circa of 35 minutes will be needed. For a higher target of 60 degree of polymerization the reaction will require at least 45 minutes to reach the 80% of conversion, and for a target of 100 it will require 60 minutes to reach the determined goal.

Monomer conversion and theoretical molecular weight has been determined by <sup>1</sup>H NMR. <sup>1</sup>H NMR analysis has been made with samples taken before the addition of the second monomer and with samples at the end of reaction. The molecular structure of PAMPTMA was characterized by <sup>1</sup>H NMR spectroscopy (Figure 10).

Also, a typical <sup>1</sup>H NMR spectrum with the assigned peaks of AMPTMA monomer can be found in Figure A.1 in Appendix A.



**Figure 10.**  $^1\text{H}$  NMR spectra of PAMPTMA in  $\text{D}_2\text{O}$ . Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments.

Monomer peaks can be found at 5.8 and 6.25 ppm (peaks *a* and *b*, respectively) corresponding to the double bond of AMPTMA (Figure A.1, Appendix A). Monomer conversion can be calculated by the ratio of the total area of the monomer peaks at 5.8 and 6.25 ppm and the polymer peaks between 3.52 and 3.10 ppm. Both integrals must be divided by the number of hydrogen protons resonance corresponding to them. Monomer conversion has been calculated using equation [8] where the monomer peaks integral was divided by 3 and the polymer integral was divided by 13.

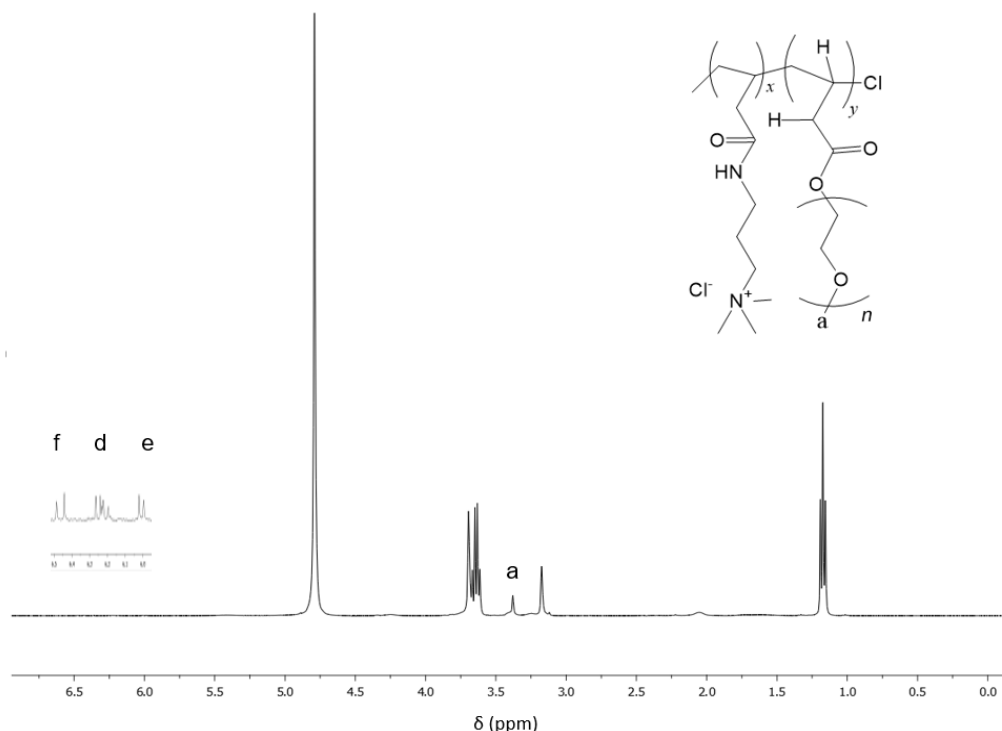
$$\text{Monomer conversion (\%)} = \left[ 1 - \frac{(\delta(5.80) + \delta(6.25)) / 3}{\delta(3.10 - 3.52) / 13} \right] \times 100 \quad [8]$$

The signal seen at 1.20 ppm belongs to the ECP initiator. For PAMPTMA polymer the peaks between 3.10 and 3.52 ppm correspond to the amine protons and to  $(\text{CH}_2\text{-N})$  connection, and are in agreement with those reported in the literature. (Mendonça et al., 2014)

For copolymer characterization, a sample has been taken just after the addition of the second monomer acting as a baseline to further calculate the OEOA monomer conversion. Also, the molecular structure of the copolymer was characterized by  $^1\text{H}$  NMR spectroscopy. A typical PAMPTMA-*b*-POEOA  $^1\text{H}$  NMR spectrum in the end of the reaction with the proton scheme adopted for the NMR spectral assignments is presented in Figure 11.

#### 4. Results and Discussion

A typical  $^1\text{H}$  NMR spectrum with the assigned peaks of OEOA monomer can be found in Figure A.2 in Appendix A.



**Figure 11.**  $^1\text{H}$  NMR spectrum of PAMPTMA<sub>52</sub>-*b*-POEOA<sub>39</sub> in D<sub>2</sub>O. Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments.

OEOA monomer peaks can be found at 6.05, 6.25 and 6.50 ppm (peaks *e*, *d* and *f*, respectively) corresponding to the double bond of OEOA (Figure A.2, Appendix A). It should be noticed that peak *d* of OEOA monomer is overlapped with the peak *b* of AMPTMA monomer at 6.25 ppm, which is not a major issue, since OEOA is only added to the reaction when AMPTMA monomer has reached a conversion over 80%. Like for AMPTMA, OEOA monomer conversion is calculated by the ratio of the total area of the monomer peaks and the polymer peak at 3.40 ppm, minus its area when the OEOA monomer was added. The area when the OEOA monomer is added to the reaction must be calculated because the OEOA polymer peak is overlapped with a peak of PAMPTMA. Also, both integrals must be divided by 3, the number of hydrogen protons resonance corresponding to them. Monomer conversion has been calculated using equation [9].

$$\text{Monomer conversion (\%)} = \left[ 1 - \frac{(\delta(6.05) + \delta(6.25) + \delta(6.50))/3}{(\delta(3.4)_1 - \delta(3.4)_0)/3} \right] \times 100 \quad [9]$$

Also, the signal seen at 1.20 ppm belongs to the ECP initiator. For OEOA polymer the peak at 3.40 ppm correspond to the protons of the CH<sub>3</sub> group like it is reported in the literature. (Mendonça et al., 2014)

All other  $^1\text{H}$  NMR spectra of PAMPTMA-*b*-POEOA can be found in Appendix B.

## 4.2 Dynamic Light Scattering (DLS)

DLS measurements were carried out to test the efficiency of the copolymers as TiO<sub>2</sub> particles stabilizers. This hypothesis was made looking for particles hydrodynamic diameter ( $D_h$ ) behaviour. This technique measures the speed that the particles are diffusing due to Brownian movement using the intensity of the scattered light by the particles and convert it to size and a size distribution.

This study has begun with the measurement of the block copolymer hydrodynamic diameter without the presence of TiO<sub>2</sub> particles. This measurement was done to verify if the block copolymers were present in the solution as unimers or aggregates.

**Table 3.**  $D_h$ , PDI and attenuator values of block copolymers and their reference determined by DLS without the presence of TiO<sub>2</sub> particles.

Block copolymer	Z-average $D_h$ (nm)	PDI	Attenuator
PAMPTMA <sub>52</sub> - <i>b</i> -POEOA <sub>39</sub>	409.0	0.508	7
PAMPTMA <sub>38</sub> - <i>b</i> -POEOA <sub>36</sub>	1 613	0.902	11
PAMPTMA <sub>30</sub> - <i>b</i> -POEOA <sub>28</sub>	708.0	0.618	11
PAMPTMA <sub>85</sub> - <i>b</i> -POEOA <sub>14</sub>	132.4	0.266	11
Additol VXW 6200	2 398	0.946	11

The results presented in Table 3 suggest the formation of aggregates ranging from 132 nm to 1613 nm. However, the value of attenuation is clearly above the reference values (<5), which indicates that the results obtained may have a considerable error associated. Further studies involving the increasing of the block copolymer concentration would be desired to understand the data obtained.

The hydrodynamic diameter evolution during the 5 days for the synthesized polymers, Additol VXW 6200 and titanium dioxide particles is presented in Table 4. Day 0 corresponds to the day that TiO<sub>2</sub> particles and polymers or Additol solution has been mixed.

**Table 4.**  $D_h$ , PDI and attenuator values of block copolymers and their reference determined by DLS in the presence of  $TiO_2$  particles during 5 days.

Block copolymer	Day 0			Day 3			Day 5		
	Z-average $D_h$ (nm)	PDI	Att.* <sup>1</sup>	Z-average $D_h$ (nm)	PDI	Att.*	Z-average $D_h$ (nm)	PDI	Att.*
PAMPTMA <sub>52</sub> - <i>b</i> -POEOA <sub>39</sub>	304.8	0.081	3	249.5	0.136	4	226.6	0.169	5
PAMPTMA <sub>38</sub> - <i>b</i> -POEOA <sub>36</sub>	304.0	0.128	3	267.6	0.187	4	205.7	0.056	5
PAMPTMA <sub>30</sub> - <i>b</i> -POEOA <sub>28</sub>	302.5	0.112	3	261.3	0.214	4	243.4	0.212	5
PAMPTMA <sub>85</sub> - <i>b</i> -POEOA <sub>14</sub>	296.3	0.115	3	249.3	0.143	4	203.2	0.058	5
Additol VXW 6200	283.5	0.073	3	218.0	0.093	4	190.9	0.078	5
$TiO_2$	277.7	0.129	3	228.2	0.114	4	197.0	0.061	4

$TiO_2$  particles have a mean size between 200-220 nm. In Table 4, the lower attenuation value indicates the presence of  $TiO_2$  particles adsorbed by the copolymers during the analysis period. Also,  $D_h$  and PDI values are comparable to the reference sample and all the copolymers values allow to conclude a good  $TiO_2$  particles stabilization with narrow particle size distribution. Nevertheless, for the 5<sup>th</sup> day PAMPTMA<sub>52</sub>-*b*-POEOA<sub>39</sub> and PAMPTMA<sub>30</sub>-*b*-POEOA<sub>28</sub> present a narrow particle size distribution, but higher than the other copolymers and the reference, which can indicate a weaker adsorption onto the pigment surface by these copolymers. This weaker adsorption can explain the higher but very acceptable  $D_h$  values for those copolymers.

A visual evaluation of the samples on the fifth day of the DLS analysis is possible in Figure C.1 in Appendix C.

From Table 4, it is also possible to observe that all copolymers have an initial  $D_h$  near 300 nm, higher than the mean size of  $TiO_2$  particles. Although, all samples have shown a decrease in  $D_h$  values indicating the sedimentation of larger particles clusters, leading to a small increase in the attenuator value. Even though, the combination of the final attenuator value and the hydrodynamic diameter value indicates the presence of stabilized particles in all the samples which can indicate that this decrease in  $D_h$  values may be also due to a slower adsorption kinetics than expected.

Additionally, it is possible to observe that all the samples have shown narrow and stable molecular weight distribution formed by the complex copolymer/ $TiO_2$  particles.

All copolymers have shown a pretty similar behavior to the reference in both  $D_h$  and PDI values indicating that PAMPTMA have strongly anchored onto the surface, overcoming the Van der Waals attractive forces between the pigment particles, and POEOA have promoted an effective steric stabilization. Looking for the results of the day 0, it is possible to conclude

<sup>1</sup> \*Att.- Attenuator

that the molecular weight of the POEOA block can influence the hydrodynamic diameter of the particles, a longer block will have a higher  $D_h$  value.

So, it is possible to conclude that all copolymers have shown an effective and good  $TiO_2$  particles stabilization. Nevertheless, both PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> and PAMPTMA<sub>85</sub>-*b*-POEOA<sub>14</sub> have exhibited more promising results presenting lower PDI values with similar  $D_h$  values to the reference.

However, a longer DLS test would be pertinent to demonstrate that the hydrodynamic diameter particle does not undergo significant change over time.

### 4.3 Zeta Potential

Colloidal dispersions stability has been evaluated through the determination of potential zeta magnitude. Zeta ( $\zeta$ ) potential must be highly positive or negative (more than 30 mV or less than -30 mV) for the particles tend to repel each other and no agglomeration occurs. (Mandzy, Grulke, & Druffel, 2005) Particles tend to agglomerate when  $\zeta$  potential value is close to zero (isoelectric point). Also,  $\zeta$  potential values for no agglomeration occurrence depend on the solvent, pH, concentration of ions and the functional groups on surface of nanoparticles. (Mandzy et al., 2005)

$\zeta$  potential measurements were performed for the copolymers in the absence and in the presence of  $TiO_2$  particles. The measurements in the absence of  $TiO_2$  particles has been made to verify the copolymers charge and to serve as basis for the samples with  $TiO_2$  particles. Their results can be evaluated in Table 5.

**Table 5.** Copolymers and Additol zeta potential values in the absence of  $TiO_2$  particles

Block copolymer	$\zeta$ Potential (mV)	Std Dev <sup>2</sup>
PAMPTMA <sub>52</sub> - <i>b</i> -POEOA <sub>39</sub>	28.3	0.40
PAMPTMA <sub>38</sub> - <i>b</i> -POEOA <sub>36</sub>	43.5	4.35
PAMPTMA <sub>30</sub> - <i>b</i> -POEOA <sub>28</sub>	38.6	3.43
PAMPTMA <sub>85</sub> - <i>b</i> -POEOA <sub>14</sub>	44.7	2.72
Additol VXW 6200	-45.0	0.93

From Table 5, it is possible to verify that PAMPTMA<sub>52</sub>-*b*-POEOA<sub>39</sub> shows a  $\zeta$  potential value in which the particles tend to agglomerate. However, the value is near the limit and the value for no agglomeration occurrence can be influenced by external factors. All the other copolymer samples and Additol show values (superior to 30 mV and inferior to -30 mV, respectively) where the particles tend to repel each other.

The charges generated on the surface will prevent agglomeration if the system is electrostatically stable. (Mandzy et al., 2005)

<sup>2</sup> Std Dev- Standard Deviation

$\zeta$  potential measurements in the presence of TiO<sub>2</sub> particles has been made in the 3<sup>rd</sup> and 5<sup>th</sup> day of the DLS analysis. Their results are summarized in Table 6. Also, titanium dioxide particles have been measured once, and their result can be found to in Table 6.

**Table 6.** Copolymers and Additol VXW 6200 zeta potential variation in the presence of TiO<sub>2</sub> particles.

Block copolymer	Day 3		Day 5	
	$\zeta$ Potential (mV)	Std Dev	$\zeta$ Potential (mV)	Std Dev
PAMPTMA <sub>52-b</sub> -POEOA <sub>39</sub>	40.2	1.00	45.4	0.55
PAMPTMA <sub>38-b</sub> -POEOA <sub>36</sub>	43.0	1.06	42.6	0.67
PAMPTMA <sub>30-b</sub> -POEOA <sub>28</sub>	42.7	0.72	44.3	0.38
PAMPTMA <sub>85-b</sub> -POEOA <sub>14</sub>	54.9	0.64	55.6	0.60
Additol VXW 6200	-61.5	0.68	-59.8	0.70
TiO <sub>2</sub>	-47.8	0.53	-	-

All samples are well above the value necessary for no agglomeration occurrence with  $\zeta$  potential values (>40 mV). Also, all of them have shown a stable behavior during the course of the study. This means that the polymers offer an effective electrostatic stabilization mechanism provided by the AMPTMA cationic polyelectrolyte block preventing agglomeration. This result suggests that this segment presents forces above the necessary to overcome Van der Waals forces of attraction between pigment particles. In general, zeta potential value in the presence of TiO<sub>2</sub> particles is higher than the value when in the absence of those particles showing that the electrostatic stabilization mechanism is more effective when in the presence of TiO<sub>2</sub> particles.

PAMPTMA<sub>85-b</sub>-POEOA<sub>14</sub> is the one that presents the best  $\zeta$  potential value. This polymer has the highest AMPTMA chain length providing the highest electrostatic stabilization. A long-term electrostatic dispersion stability will imply the maintenance of the  $\zeta$  potential values above the values referenced before.

#### 4.4 Paint Formulation Performance

This part of the project involved the participation of Resiquímica where all synthesized copolymers have been tested in a paint formulation and compared with the reference, Additol VXW 6200.

PAMPTMA<sub>85-b</sub>-POEOA<sub>14</sub> sample has not been tested because it has turned into a gel when Texanol (ester) was added to the paint formulation. Before the evaluation of the copolymers performance when in a paint formulation, an *Hegman* test has been made to the copolymer samples to evaluate the quality of the dispersion. *Hegman* gages are used to control the production, storage, and application of dispersion products produced by milling in the paint, plastic, pigment, paper, and many other industries. To do this test an excess of sample is placed in the deep end of the groove, and with a straight-edge scraper, the sample is dragged toward the shallow end of the groove. Ratings are made in terms of the point on the scale where the oversize particles first appear in substantial concentration. The rating scale ranges from 0 to 8 Hegman, depending on the particle size (increases as the particle size decreases). Flat paints



have a typical dispersion of around 5 Hegman. All the copolymer tested presented an Hegman value of 7, therefore have passed this test.

The characteristics measured to evaluate the copolymers performance in a paint formulation are presented in Table 7. The reference white in CIELab parameters values are  $L^* = 100$ ,  $a^* = 0$ , and  $b^* = 0$ .

**Table 7.** Properties of a paint formulation containing different polymers as stabilizing agent.

Characteristics	Additol VXW 6200	PAMPTMA <sub>52-b</sub> - POEOA <sub>39</sub>	PAMPTMA <sub>38-b</sub> - POEOA <sub>36</sub>	PAMPTMA <sub>30-b</sub> - POEOA <sub>28</sub>
<b>CIELab Parameter</b>				
L	98.08	97.62	98.08	97.98
a	-0.90	-0.95	-0.92	-0.92
b	1.23	1.05	1.21	1.21
<b>Brightness (u.b.)</b>				
∠ 20°	11.8	-	17.8	12.0
∠ 60°	41.7	-	49.2	41.9
∠ 85°	72.5	-	76.6	71.1
<b>Contrast Ratio (%)</b>	95.91	-	95.80	94.87
Dry film thickness (μm)	78	-	80	27
<b>Solid content (%)</b>	57.2	57.4	57.1	56.7
<b>Initial Viscosity</b>				
ICI Cone&Plate at 25°C (P)	1.6	4.3	2.8	2.0
Stormer at 23°C (KU)	91	>150	104	102
Brookfield at 23°C H5/6, 20rpm (mPa.s)	7 800	36 250	12 000	11 300
Specific Gravity at 23°C	1.319	1.300	1.317	1.316
<b>Viscosity after 28 days at</b>				
Stormer at 23°C (KU)	86			
Brookfield at 23°C H#, 20rpm (mPa.s)	5 000	Gel	Gel	Gel

PAMPTMA<sub>52-b</sub>-POEOA<sub>39</sub> sample has turned into a gel 48 hours after the paint formulation production making impossible to measure its brightness, contrast ratio and dry film thickness, which can indicate that copolymers with AMPTMA chain length below DP=52 can be more stable in a paint formulation.

CIELab, brightness and contrast ratio parameters have been tested during this performance evaluation. The chromatic coordinates and the contrast ratio have not shown big differences between the polymers samples and Additol. However, the copolymers have shown

#### 4. Results and Discussion

to be more brightener than the reference. The brightness is an attribute that indicates how well a surface reflects light and is an indicator of pigment distribution, because it increases for better dispersed systems. (Farrokhpay et al., 2010) PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> was the brightest sample with better results than Additol, indicating a better pigment dispersion. Nevertheless, PAMPTMA<sub>30</sub>-*b*-POEOA<sub>28</sub> and PAMPTMA<sub>52</sub>-*b*-POEOA<sub>39</sub> also indicates a good pigment dispersion having a similar behavior to the reference regarding to the paint brightness characteristics, but as mentioned above, PAMPTMA<sub>52</sub>-*b*-POEOA<sub>39</sub> have turned into a gel after 48 hours.

Both solid content and specific gravity at 23°C have returned similar results to Additol VXXW 6200 when tested.

Copolymers samples have shown higher initial viscosity than the reference. Also, polymer molecular weight has shown to have a strong influence in the viscosity of the paint formulation. A higher molecular weight will lead to a higher viscosity. After being stored for 28 days at 50°C all copolymer samples have turned into a gel showing that this paint formulation presents stability over time issues that must be studied because PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> presented a very promising result for the 60° brightness.

PAMPTMA-*b*-POEOA block copolymers promotes an electrosteric mechanism of stabilization. A good pigment dispersion will provide a better gloss and hiding power to the paint formulation. Also, a higher polymer molecular weight will lead to a more viscous paint formulation.

## 5. Conclusions and Future Works

### 5.1 Conclusions

PAMPTMA-*b*-POEOA block copolymers with controlled structure and different molecular weight were synthesized in order to investigate their performance in TiO<sub>2</sub> pigment stabilization and dispersion in aqueous medium.

After copolymers synthesis, they have been analysed through DLS and  $\zeta$  potential measurements. All the block copolymers present promising results in these tests with hydrodynamic diameters between 200 and 245 nm after 5 days and  $\zeta$  potential above 40 mV, indicating that they successfully stabilize TiO<sub>2</sub> particles, and the suspension have a good dispersion stability. Nevertheless, in the beginning of the DLS test it was found that for higher molecular weights of POEOA block, the hydrodynamic diameter of the particles increased. Yet, during the DLS test both PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> and PAMPTMA<sub>85</sub>-*b*-POEOA<sub>14</sub> have exhibited similar  $D_h$  values to the reference with low PDI values.

CIELab parameters, brightness, contrast ratio, storage stability and viscosity were analysed incorporating the copolymers in a paint formulation. However, PAMPTMA<sub>85</sub>-*b*-POEOA<sub>14</sub> has turned into a gel in the paint formulation production which turned impossible to test this copolymer when applied in a paint formulation. Also, 48 hours after the paint formulation production PAMPTMA<sub>52</sub>-*b*-POEOA<sub>39</sub> sample has turned into a gel and it has not been characterized regarding the paint brightness, dry film thickness and contrast ratio. PAMPTMA<sub>30</sub>-*b*-POEOA<sub>28</sub> and PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> presented similar results to the reference regarding to CIELab parameters and contrast ratio. Also, PAMPTMA<sub>30</sub>-*b*-POEOA<sub>28</sub> have a similar behavior to the reference regarding to the paint brightness. However, PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> have better brightness results than the reference indicating that this copolymer disperses better the pigment particles. All the copolymers samples have higher viscosity than Additol VXW 6200, and a positive relation between the copolymer molecular weight and the viscosity has been observed. The samples have turned into a gel after being stored for 28 days, indicating that the samples cannot provide stability over time as TiO<sub>2</sub> pigment stabilizers.

### 5.2 Future Work

As future work, it would be important to synthesize different block copolymers having one segment of PAMPTMA or POEOA to study their differences and compare with PAMPTMA-*b*-POEOA. For example, synthesize mPEG-*b*-PAMPTMA to study the difference between the hydrophilic groups or PAETAC-*b*-POEOA and mPEG-*b*-PAETAC to compare with AMPTMA and also to evaluate the difference between OEOA and PEG chain block.

For the synthesized polymers, Transmission Electron Microscopy (TEM) analysis would be important to prove that they strongly adsorb onto the titanium dioxide surface and no agglomeration occurs between the pigment particles.

## 5. Conclusions and Future Works

Also, PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> (the sample with a promising 60° brightness result) should be tested again in a longer DLS test to demonstrate that the hydrodynamic diameter particle does not undergo significant change over time.

## 6. References

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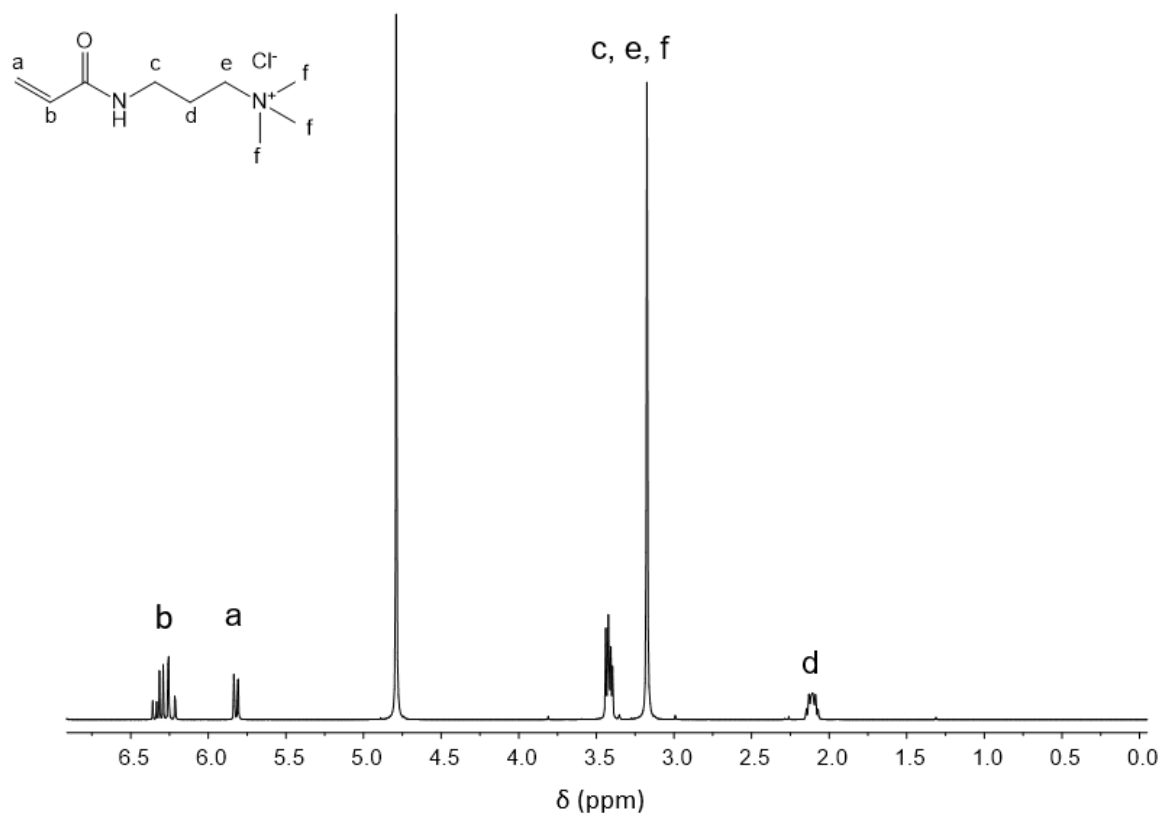
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## Appendix

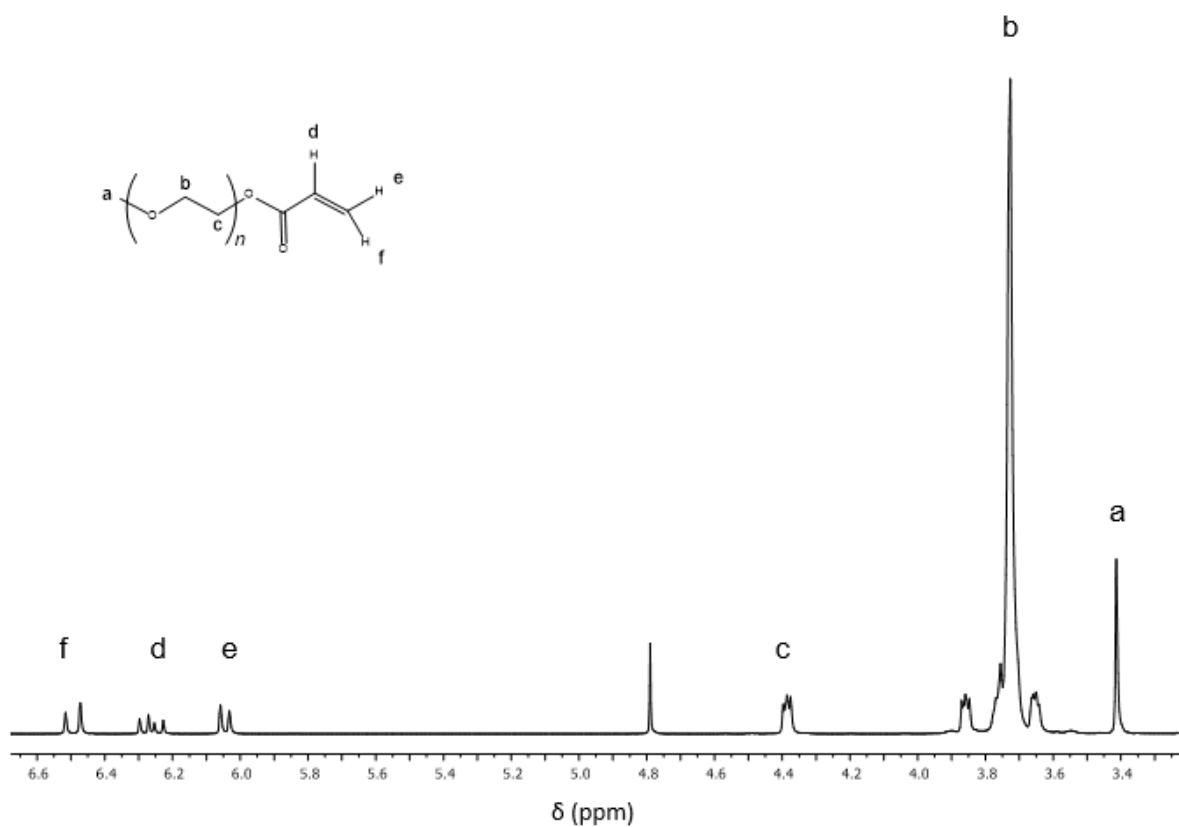
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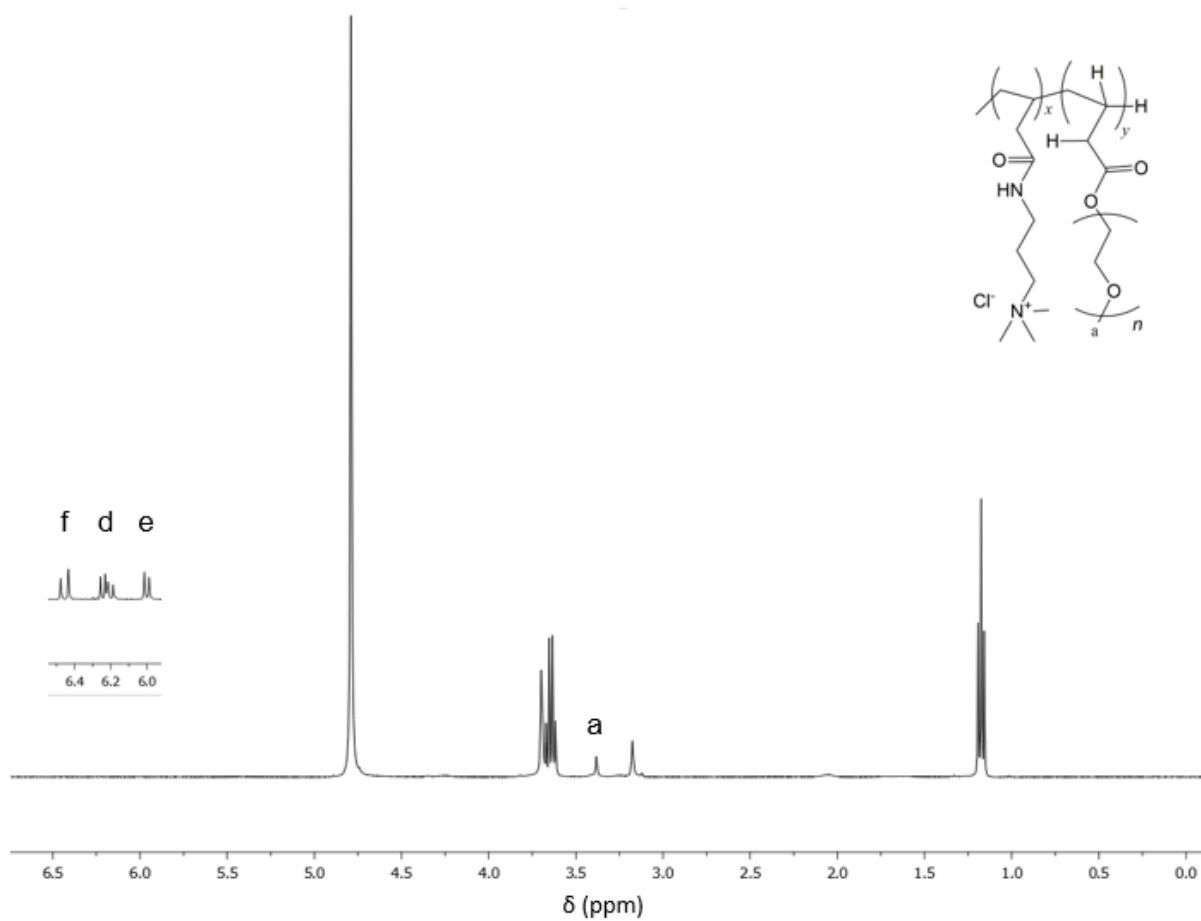
Appendix A – Monomers  $^1\text{H}$  NMR spectra

**Figure A.1.**  $^1\text{H}$  NMR spectrum of AMPTMA in  $\text{D}_2\text{O}$ . Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments.

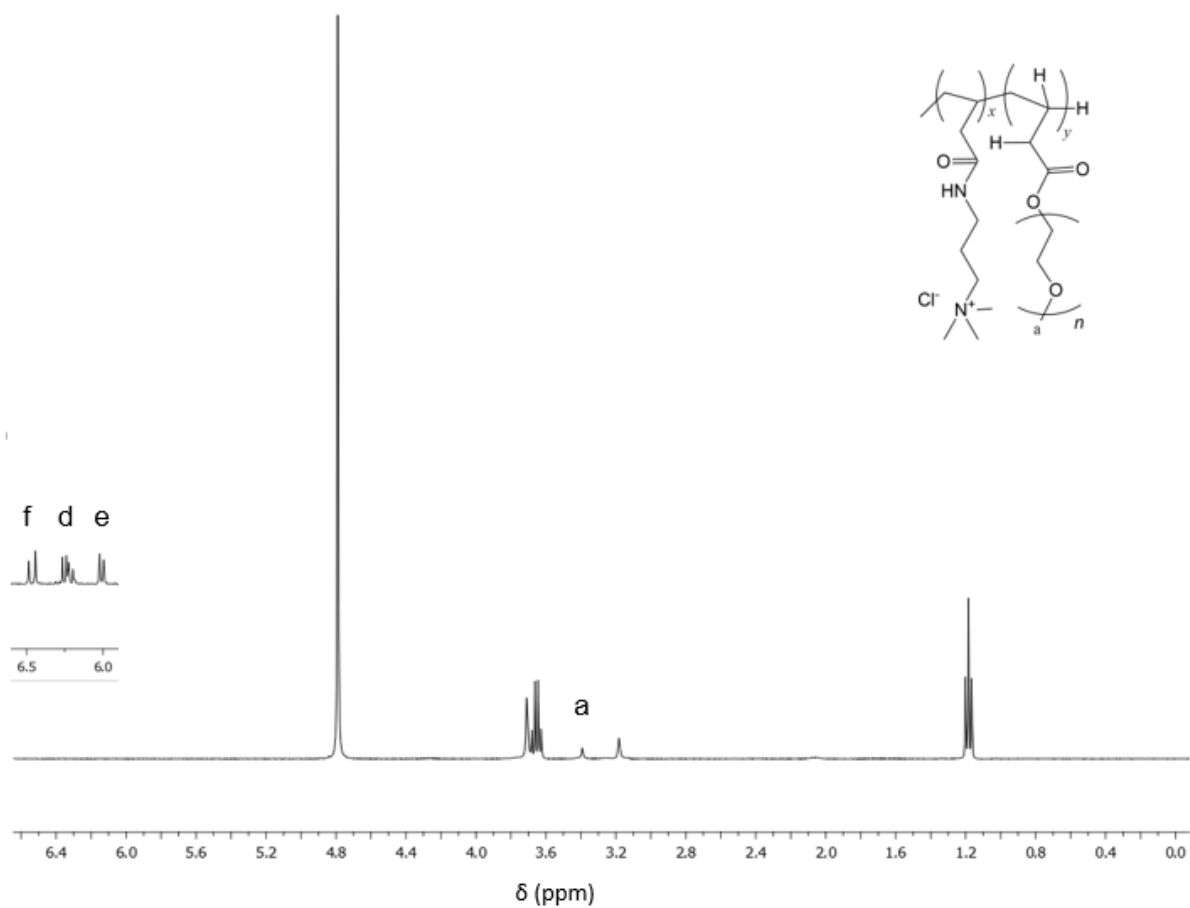




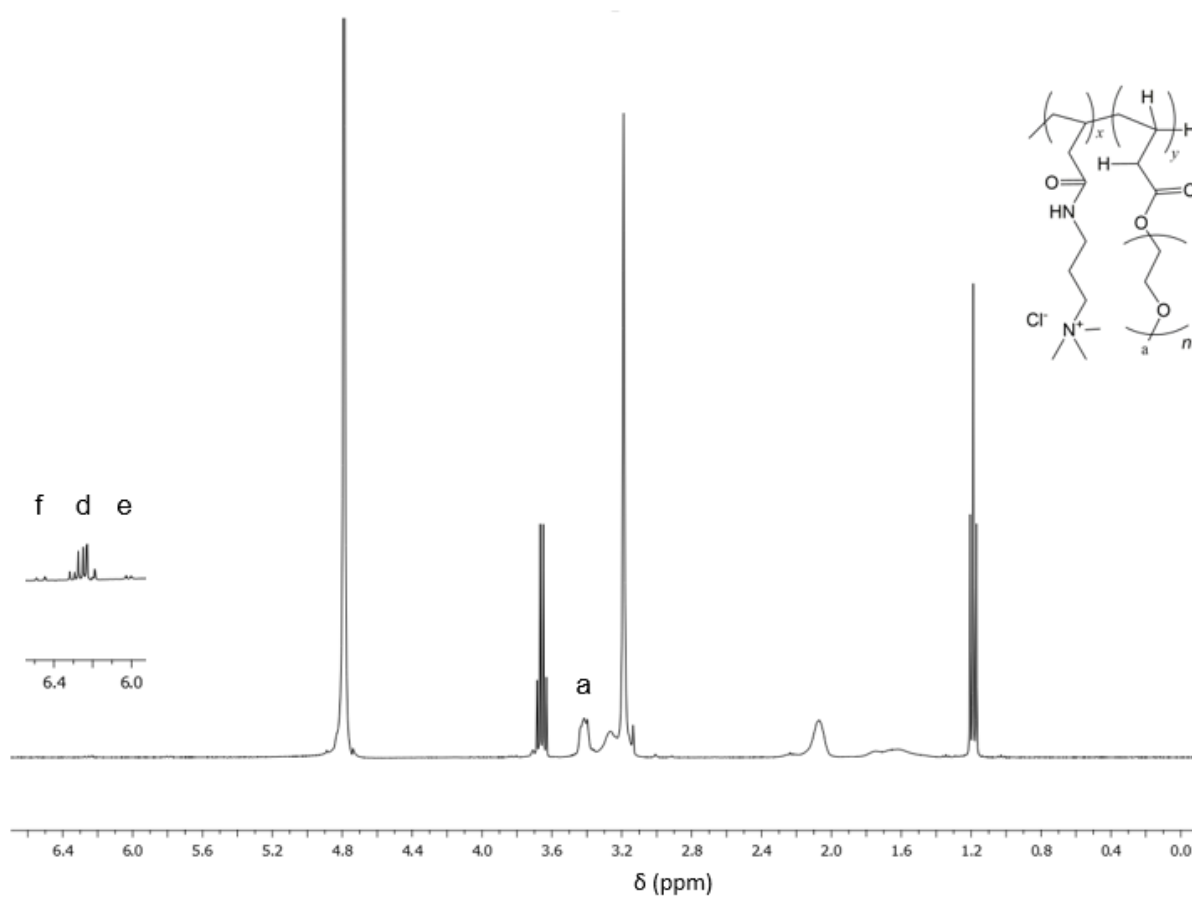
**Figure A.2.**  $^1\text{H}$  NMR spectrum of OEPA in  $\text{D}_2\text{O}$ . Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments.

Appendix B – Copolymers  $^1\text{H}$  NMR spectra

**Figure B.1.**  $^1\text{H}$  NMR spectrum of PAMPTMA<sub>38</sub>-*b*-POEOA<sub>36</sub> in  $\text{D}_2\text{O}$ . Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments.

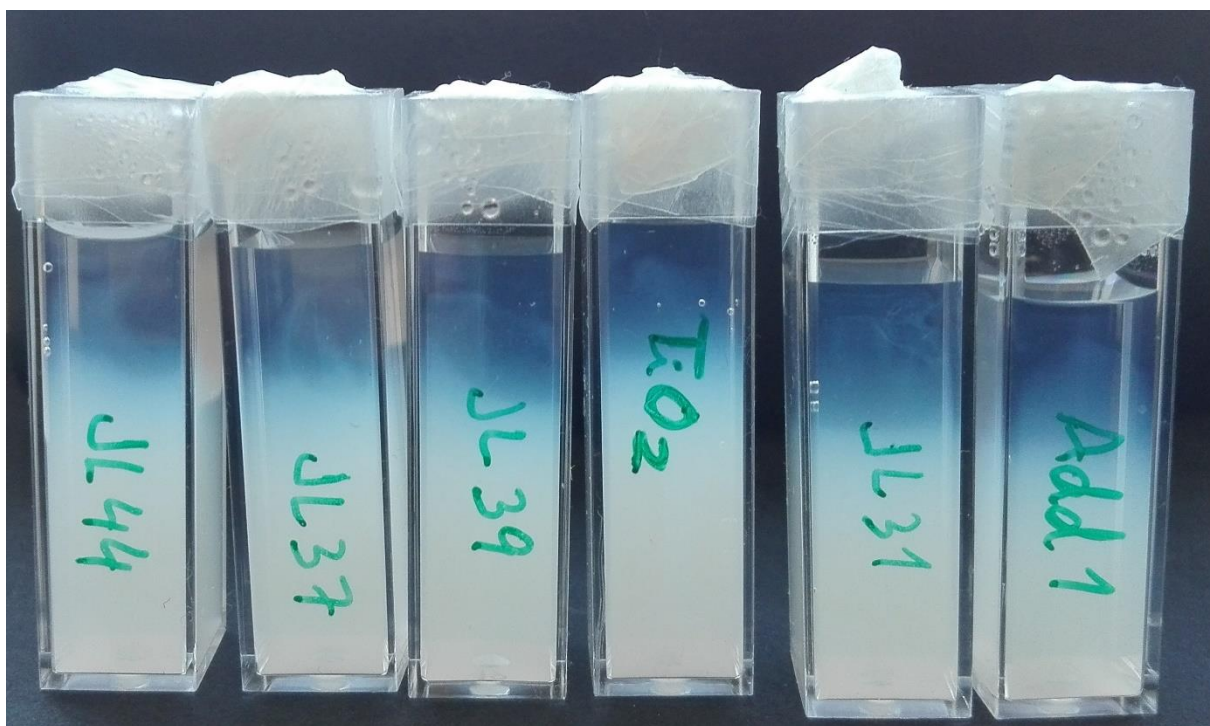


**Figure B.2.**  $^1\text{H}$  NMR spectrum of PAMPTMA<sub>30</sub>-*b*-POEOA<sub>28</sub> in  $\text{D}_2\text{O}$ . Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments.



**Figure B.3.**  $^1\text{H}$  NMR spectrum of PAMPTMA<sub>85</sub>-*b*-POEOA<sub>14</sub> in  $\text{D}_2\text{O}$ . Their chemical structure and the proton identification scheme adopted for the NMR spectral assignments.

## Appendix C – DLS samples



**Figure C.1.** Photos of  $\text{TiO}_2$  suspensions on the 5<sup>th</sup> day. From left to right:  $\text{PAMPTMA}_{85}\text{-}b\text{-POEOA}_{14}$ ,  $\text{PAMPTMA}_{38}\text{-}b\text{-POEOA}_{36}$ ,  $\text{PAMPTMA}_{30}\text{-}b\text{-POEOA}_{28}$ ,  $\text{TiO}_2$ ,  $\text{PAMPTMA}_{52}\text{-}b\text{-POEOA}_{39}$ , Additol VXW 6200.