

Synthesis of PE-based nanoparticles from an original surfactant-free emulsion polymerization process of ethylene using RAFT technique

Ricardo Silva, Frank D'Agosto¹, Muriel Lansalot¹, Vincent Monteil¹, Maria do Rosário Ribeiro²

¹ *Laboratory of Chemistry, Catalysis, Polymers and Processes (C2P2 – UMR 5265), Université de Lyon*

² *Institute for Biotechnology and Bioengineering (IBB), Instituto Superior Técnico (IST), Universidade de Lisboa*

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Abstract. Taking advantage of the recently established controlled radical polymerization of ethylene mediated by xanthates and the expertise of the C2P2 team in the emulsion polymerization of ethylene, this thesis is a contribution to the study of the synthesis of polyethylene-based nanoparticles by implementation of reversible addition-fragmentation chain transfer (RAFT) polymerization of ethylene in the emulsion process from water-soluble functional polymers. The mechanism of particle formation proceeds without surfactants by polymerization-induced self-assembly of amphiphilic block copolymers (PISA process). The first part of this project consisted in the synthesis and purification of the macroRAFT (polyethylene glycol end-functionalized with xanthate, PEG-X) used in the polymerizations mediated by xanthates, which was prepared by post-modification of an existing polymer. The characterization of the resulting product validated its properties, which allowed to proceed to the polymerization procedures. To evaluate the effect of the presence of PEG-X in the ethylene polymerization several polymerizations were performed at 70°C and 100 bar of ethylene pressure, with and without surfactant, in the presence of either the macroRAFT agent or its non-functional counterpart (PEG-OH). It was found that indeed the polymerizations were strongly influenced by the presence of the macroxanthate. In addition, it appeared that the macroRAFT/initiator molar ratio strongly influenced the yield of PE. A kinetic study of the polymerization in the presence of the macroRAFT agent (at 70°C) was performed at two different pressures (100 and 200 bar). The increase in pressure appeared to affect the stabilization of the obtained latexes, particularly for long polymerization times.

Keywords. Polyethylene, free radical emulsion polymerization, RAFT, MADIX, PISA.

Introduction

Polyethylene, PE, is the simplest and most produced polymer in the industry of synthetic polymers. Considered a commodity, the production of PE reached around 78 Million tons in 2012. ^[1]

The polymerization of ethylene can be performed either by free radical polymerization, FRP, which requires the use of radical initiators and is normally performed at high pressure (1000-4000 bar) and high temperature (200-300°C), or by a catalytic route, using organometallic catalysts, which normally requires much lower pressures (1-50 bar) and temperatures ($\approx 100^\circ\text{C}$). ^[2] The FRP process originates branched polymer chains with long and short chain branches, whereas organometallic coordination catalysts lead to linear or regularly branched polymer chains. The polymerization of ethylene can be carried out in solution, slurry or in bulk, and at pressures above 100MPa, ethylene is in its supercritical state ($T_{\text{crit}}=9,2^\circ\text{C}$, $P_{\text{crit}}=50,4\text{ bar}$) ^[3] acts as solvent for polyethylene. ^[4]

Until recently, it was common knowledge that the LDPE production process could only be performed efficiently under very harsh condition. However, the C2P2 team reported that the FRP of ethylene using a

thermal initiator under milder conditions ($<100^\circ\text{C}$ and $<300\text{ bar}$), which allowed studying ethylene polymerizations using classical radical initiators, such as diazo compounds (2,2'-Azobisisobutyronitrile (AIBN) for example. ^[5] ^[6], ^[7]

The effect of the solvent in the FRP of ethylene was studied at the C2P2. Indeed, the solvent has a major influence on the polymerization activity and on the molecular weight of the obtained PEs. Either low molecular weight and high chain-end functionality or non-functional/higher molecular weight PEs can be synthesized according to the solvent used. ^[6], ^[7] A number of organic solvents were studied. It was found that the nonpolar ones were less efficient than the polar ones. Some of the solvents (particularly THF, DMC and DEC) showed interesting yields or molar masses.

The potential transposition of this FRP of ethylene to low transferring solvents (including water), while keeping activity as high as possible was investigated at C2P2. DMC showed to be an excellent compromise for this process, being the less transferring polar solvent and more efficient than nonpolar solvents, leading to high molar mass PEs and acceptable yields. ^[7] ^[8]

As a non-transferring and polar solvent, water was also investigated. An emulsion polymerization in aqueous dispersed would also benefit from the compartmentalization of radicals. The experiments led to the formation of PE latexes. The initial studies at C2P2 involved a cationic system using a water-soluble initiator, 2,2-azobis(2-midinopropane) dihydrochloride (AIBA) in water at 70 °C, with and without surfactant (cetyltrimethylammonium bromide, CTAB), which was used to help nucleation and particle stabilization. The stabilization of PE particles in the system without surfactant was ensured by the cationic fragments of the initiator, which induced electrostatic repulsion.^[9]

In both cases (with/without surfactant) stable PE latexes and significant yields were attained for ethylene pressures from 50 up to 250 bar. For 4h of polymerization time the surfactant-free system yielded 1.3 g of PE, higher than in some organic solvents. The particle were spherical and their diameter increased with the ethylene pressure from 30 to 110 nm with very low polydispersity indexes, *PDI* (≈ 0.05).

In the presence of CTAB the yield increased to 4.6 g of PE. The average particle size plateaued at 50 nm with *PDI* were close to 0.1 and the particles showed a disc-like morphology.

In both cases the yield and molar masses increased with the ethylene pressure. However the activities observed with surfactant were much higher than the surfactant-free polymerization and were found to be even higher than the ones achieved in THF.^[6] Particle sizes increased, but their shape remained unchanged. The emulsion polymerization yielded PEs with high molar masses ($M_n \approx 10^4$ to 10^5 g mol^{-1}) and the PEs were moderately branched. The higher branching level in water than in an organic solvent was explained by the compartmentalization of the radicals, which increased the possibility of transfer reactions to the polymer.

The FRP process can be used to (co)polymerize a large variety of monomers with a large range of polymerization conditions. However, FRP provided a poor control of the molar mass of the polymer, its dispersity, the end functionality and the architecture of the chains.^{[2], [10]}

The most common techniques to control FRP are the *Nitroxide-Mediated Polymerization* (NMP), the *Atom Transfer Radical Polymerization* (ARTP), and the *Degenerative Transfer* (DT) or the *Reversible Addition-Fragmentation Chain Transfer* (RAFT). This last technique was used in the frame of this work is detailed in the following paragraphs.

Since its disclosure, the RAFT process has been the most versatile of the CRP techniques, as it can be

used with a large range of monomers resulting in polymers with controlled molar masses and narrow molar mass distributions ($\mathcal{D} < 1.2$).^[11]

The RAFT process requires the use of an organic molecule, called RAFT chain-transfer agent (CTA), which is a thiothiocarbonylated compound (ZC(=S)SR) (Z-activating group/R leaving group). It can be for example: trithiocarbonate ($\text{Z} = \text{-S-R'}$), dithioester ($\text{Z} = \text{-R'}$), dithiocarbamate ($\text{Z} = \text{-NR'R''}$) or a dithiocarbonate (also called xanthate) ($\text{Z} = \text{-OR'}$). The process with a xanthate has also been described as *MADIX (Macromolecular Design via Interchange of Xanthate)* simultaneously to RAFT.^[12]

The mechanism of RAFT process involves the typical reactions of a conventional FRP, plus additional addition-fragmentation steps. In the early stages of the polymerization, the addition of the propagating radical (P_n^\bullet) to the RAFT agent followed by the fragmentation of the intermediate radical species, gives rise to a polymeric RAFT agent, or macroRAFT agent, and a new radical (R^\bullet) forming a pre-equilibrium (Figure 1).

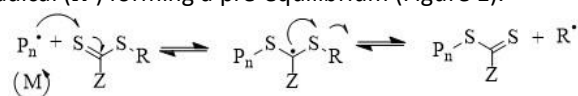


Figure 1 -Addition to RAFT agent.

The radical R^\bullet reinitiates the polymerization by addition to the monomer forming a new propagating radical (P_m^\bullet). This step continues in the presence of the monomer, generating an equilibrium between the active species that carry on with the polymerization (P_n and P_m) and with the dormant ones, allowing the polymeric chains to grow at the same rate (Figure 2). This is responsible for the narrow molar mass distribution of the resulting polymers.

The CTA is thus responsible for the equilibrium between the dormant and active chains and its choice is a critical point in RAFT polymerization.

An adequate RAFT agent should be selected depending on the monomer to polymerize. According to their reactivity, monomers can be divided into two groups: more-activated monomers (MAMs) and less-activated monomers (LAMs). The first group typically includes monomers with vinyl groups conjugated with a carbonyl group or an aromatic ring (for example, (meth)acrylates and styrenics), while the second group typically contains a saturated alkene or oxygen/nitrogen lone pair adjacent to the vinyl group. In LAM group are included such monomers as ethylene and vinyl acetate (VAc). Several reviews have provided guidance for selecting the ideal RAFT agents for most monomers.^{[13], [14]}

The reactivity of a CTA during RAFT is strongly affected by both the Z and R groups. The structure of

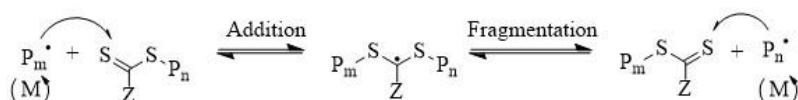


Figure 2 - Chain equilibration by reversible addition fragmentation.

the Z group is indeed very important. It governs the general reactivity of the C=S bond toward radical addition and affects the lifetime/fate of the resulting intermediate radical. The R group, should be a good homolytic leaving group, being more stable than P_n^{\cdot} , in order to be formed and be able to reinitiate the polymerization.^[15]

Dithioesters or trithiocarbonates suitable for controlling polymerization of MAMs, inhibit or retard polymerizations of LAMs due to the poor ability of the radical leaving-group to propagate species with a terminal LAM unit.^{[16],[13]} Similarly RAFT agents suitable for controlling polymerizations of LAMs, such as xanthates, tend to be ineffective with MAMs. The reduced effectiveness of the dithiocarbamate RAFT agents with MAMs relates to their lower reactivity toward radical addition and smaller transfer constants. The double-bond character of the thiocarbonyl is reduced by the contribution of zwitterionic canonical forms that localize a positive charge on nitrogen and a negative charge on sulfur.^[13]

With the recent progress from the C2P2 team in efficiently performing the FRP of ethylene under mild conditions, and considering ethylene as a LAM, the team investigated the RAFT polymerization of ethylene and reported the first example of CRP of ethylene through RAFT mediated by xanthates.^[17]

DMC was used as solvent to minimize irreversible chain-transfer reactions while maintaining an acceptable yield. The polymerizations were thus performed in DMC with AIBN as initiator at 200 bar and 70°C. A linear increase of M_n versus the yield was observed and much narrow molar mass distributions evidencing a living character.

The emulsion polymerization process requires the use of surfactants that may be detrimental to the final application. Amphiphilic block copolymers can be employed as surfactants. Thus, finding alternatives in which surfactant is both produced in situ and covalently anchored at the surface of the final particles was very appealing.

With the developments of the CRP in water, emulsion polymerization can be now performed according to the polymerization-induced self-assembly (PISA) process. The basic principle behind this process is to grow a hydrophilic living polymer chain in a first step and chain-extend it in water with a hydrophobic monomer, creating block copolymers that will self-assemble into nano-sized self-stabilized particles (Figure 3). The PISA process can lead to various morphologies (worms, rods, fibers, etc.).^[18]

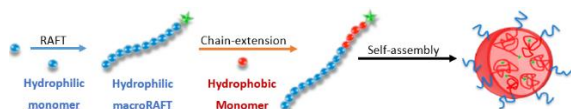


Figure 3 - PISA using RAFT in aqueous system.

The C2P2 team recently managed to perform PISA using RAFT according to a one pot process where the hydrophilic and the hydrophobic block are formed successively in the same reactor in water.^[18]

First developed with trithiocarbonate CTAs, suitable to polymerize more-activated monomers such as styrene, n-butyl acrylate and methyl methacrylate as hydrophobic monomers, the C2P2 team recently showed that a xanthate-based PISA process could also be performed and LAMs such as VAc could be employed as hydrophobic monomer.^[19]

Hence, gathering the knowledge developed at C2P2 in the chemistry fields presented above, namely the FREP of ethylene under mild condition, its CRP by RAFT, the polymerization-induced self-assembly (PISA) process the foundations were laid for the project investigated in this work: The synthesis of PE-based nanoparticles from an original surfactant-free emulsion polymerization of ethylene using RAFT technique.

Experimental section

Materials

2,2'-Azobis (2-methylpropionamide) dihydrochloride (AIBA, 97%) was used as initiator and cetyl trimethylammonium bromide (CTAB, 99%) as surfactant, both from Sigma-Aldrich®.

The macroRAFT agent used in this work, the poly(ethylene glycol) functionalized with a xanthate chain end (PEG-X) was obtained by post-modification of a commercial poly(ethylene glycol) methyl ether (PEG, M_n 2000 g mol⁻¹, Sigma-Aldrich®), by a xanthate extremity. 2-bromopropionyl bromide (97%) and triethylamine (≥99.5%) from Sigma-Aldrich® were also used in this process. The monomer used in the polymerizations was ethylene from Air Liquide (99.95 %).

Synthesis of the macroRAFT agent – PEG-X

The macroRAFT synthesis was performed in two steps. The first step involved the dissolution of the PEG-OH in dichloromethane (DCM) and triethylamine (TEA) was added to the mixture. 2-bromopropionyl bromide was added drop-by-drop, with the flask in an ice bath. After this addition, the flask was removed from the ice bath and left under stirring for 16 h. The secondary products, salts of hydrobromic acid (HBr), were separated from the product by filtration. The product was then washed with a series of solutions: first a saturated aqueous solution of NH₄Cl, followed by NaHCO₃ and then by water. The aqueous and the organic phases were separated, and the latter was further dried out using magnesium sulphate and filtered. The solvent was evaporated and the residue dried up to constant weight.

In the second step, the product from the first step was dissolved in DMC and O-ethyl xanthic acid potassium salt was slowly added and left overnight for

stirring. The product was purified, removing the formed KBr by filtration, and was washed two times with a saturated aqueous solution of NH_4Cl , followed by NaHCO_3 and after with water. The phases were separated and the organic one was dried using magnesium sulphate. After filtration, the resulting solution was precipitated in petroleum ether in an ice bath and the recovered product was dried under vacuum.

High pressure polymerization

The polymerizations were performed in an apparatus designed at C2P2. The reactor was a 160 mL stainless steel autoclave, capable of withstanding temperatures of 150°C and pressure up to 250 bar, from *Parr Instrument Company*.

Polymer characterization

To determine the polymer content (PC) of the latex, a sample of the latex was dried and the masses of non-PE species were subtracted from the total mass allowing the determination of the polymerization yield. In the case of formation of coagulated polymer the yield was calculated from the polymer content of the latex part and the mass of coagulated polymer.

Molar mass measurements

Polymer molar masses were measured by size exclusion chromatography (SEC) in a Viscotek Malvern® HT-GPC Module 350 A obtaining the number-average molar mass, M_n and the weight-average molar mass, M_w and subsequently the *dispersity* ($D = M_w/M_n$).

Differential Scanning Calorimetry (DSC)

The melting and crystallization temperatures (T_m and T_c) and crystallinity (X_c and X_m) were obtained by Differential Scanning Calorimetry (DSC) on an equipment from Mettler-Toledo where a crucible (40 μL , Al) was filled with dried samples, which were submitted to two successive heating and cooling cycles (from 10°C to 160°C at a 5°C min^{-1} rate and from 160°C to 10°C at a rate of $20^\circ\text{C min}^{-1}$).

Colloidal analyses

The particle size was obtained by performing Dynamic Light Scattering (DLS) on a Zetasizer Nano ZS, which also allowed the determination of the polydispersity index, *PDI*. The scattered signal intensity was analysed at a 173° angle, at 25°C .

Nuclear Magnetic Resonance (NMR)

To analyse the structure of the products obtained in this work ^1H NMR analyses in CDCl_3 were performed on a Bruker Avance II (400 MHz) available at the C2P2 laboratory.

Transmission Electron Microscopy (TEM)

The TEM analyses were performed at the *Centre Technologique des Microstructures, Ctμ, Lyon 1, Université Claude Bernard (Villeurbanne, France)* on a Philips CM120 transmission electron microscope capable of supplying tensions between 60 and 120 kV.

Results and Discussion

PEG-X synthesis

The NMR spectrum of the PEG-X revealed that the obtained structure for this molecule was consistent with the data from other studies where this macroRAFT was synthesized. [19] (Figure 4)

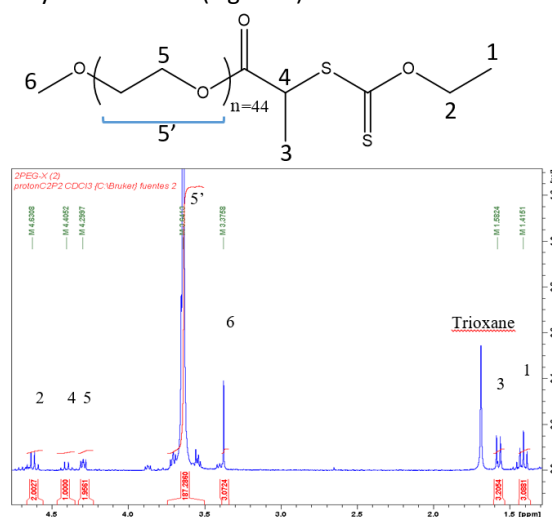


Figure 4 - ^1H NMR of PEG-X in CDCl_3 .

The Size Exclusion chromatography (SEC) was performed in THF and permitted to obtain the molar mass of the macroRAFT agent and its dispersity, being respectively, 2300 g mol^{-1} and 1.03.

The PEG-X was thus analysed by DSC allowing the evaluation of the melting temperature, T_m , and the crystallization temperature, T_c , as well as the crystallinity values (X_c and X_m). As seen in the following figure, the crystallization was identified in the exothermic curve and the melting temperature was identified in the endothermic curve. It was observed a rather high crystallinity, around 47 %, and a T_m of around 50°C , a value very close to the one that characterizes polyethylene glycol methyl ether, 52°C .

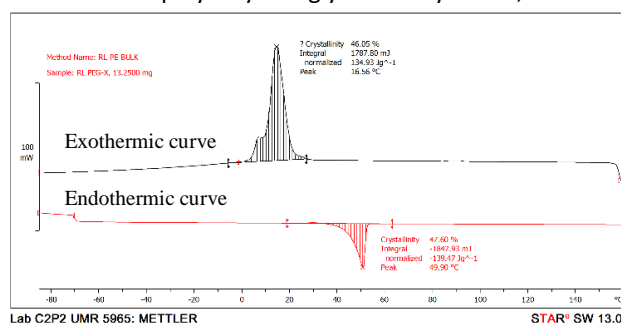


Figure 5 -DSC analyses of PEG-X.

Free radical emulsion polymerization of ethylene

The first sets of experiments were performed to verify the experimental methodology and more importantly to establish references to the experiments performed in the presence of the PEG-X. The reference experiments included polymerizations carried out in water 1) with the initiator only, 2) with both initiator and surfactant, and 3) with initiator and the commercial PEG (PEG-OH), and the major features that characterize each of these polymerization systems were compared with that observed for the polymerization performed in the presence of initiator and PEG-X.

Works on free radical emulsion polymerization of ethylene showed that a cationic initiating and stabilizing system was suitable. AIBA and CTAB were thus selected as water-soluble initiator and surfactant, respectively.

Ethylene pressure was fixed to 100 bar at the beginning of the process and maintained with small additions of ethylene into the reactor as it was consumed during the polymerization (4h). The stirring rate was set to 250 rpm and the temperature at 70°C, being sufficient to guarantee a decomposition rate of AIBA that ensured a reasonable reaction rate (AIBA, $k_d = 1,9 \times 10^{-3} s^{-1}$ in water at 69°C). [20] The initial solution was charged with AIBA and depending on the desired polymerization, others species could be added (CTAB, PEG-OH or PEG-X). The quantity of CTAB (1 g L⁻¹) was selected to be three times above the value of the Critical Micelle Concentration (0,3 g L⁻¹). The polymerization of ethylene in the presence of PEG-OH, allowed us to set a reference to evaluate the influence of the xanthate chain-end. The references of the four representative experiments to be compared are:

- RL-PE 18 selected as the blank experiments (performed only with AIBA initiator);
- RL-PE 20 for the polymerizations performed with AIBA and surfactant (CTAB);
- RL-PE-14 for the polymerizations performed with AIBA and PEG-OH;
- RL-PE 09 for the polymerizations performed with AIBA and PEG-X.

Comparison between the appearance of the different types of polymerization

The appearance of the obtained latexes was observed to evaluate their stability. The four different polymerizations produced stable latexes. According to the similar aspect of the produced latexes they were divided in two groups of experiments.

The polymerization performed only with the AIBA yielded a milky stable white latex, as observed in Figure 6–[1], similarly to the latex produced in the polymerization performed with PEG-OH (Figure 6–[3]). The polymerization with surfactant, CTAB, (Figure 6–[2]) yielded latexes with a translucent aspect, which

were very similar to the ones obtained in the presence of PEG-X (Figure 6–[4]). The appearance of the obtained latexes can be an indicator of the particles size present in the samples. A milky latex aspect usually indicates the presence of large particle (≈ 100 nm) and a translucent one indicates the presence of smaller particles size (≈ 20 nm).

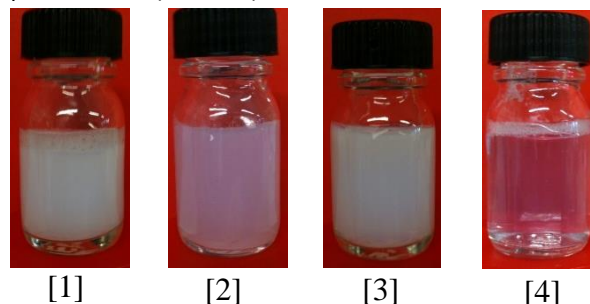


Figure 6 - Latexes obtained by FREPE (1- Blank; 2 - CTAB; 3 - PEG-OH; 4- PEG-X) (4h, 50 mg AIBA, 250 rpm, T=70°C, and P_{ethylene}≈100 bar).

Comparison between the yields of the four types of polymerization

Table 1 presents the yields of the different types of polymerization for the same polymerization time, 4 hours, sorted by increasing order of values.

Table 1 - Yields for the different types of polymerizations (4h, 50 mg AIBA, T=70°C, and P_{ethylene}≈100 bar).

Polymerization Type	Name of sample	Quantity (t)	Yield (g)/PC (%)
Polyethylene Glycol Xanthate (PEG-X)	RL-PE 09	0.3 g	0.5/0,9
Without surfactant (Blank)	RL-PE 18	--	0.6/1,2
Polyethylene Glycol (PEG-OH)	RL-PE 14	1 g	0.6/1,2
With surfactant (CTAB)	RL-PE 20	50 mg	2.6/5.0

(1) - Mass of the referenced compounds introduced in the initial solution (CTAB, PEG, PEG-X).

The polymerization carried out with CTAB, achieved the highest yield, similar to the ones reported in previous studies. [9] In addition, the surfactant-free polymerization also presented similar values to the ones from former studies, indicating a good reproducibility for the polymerization methodologies.

The surfactant-free experiment and the one performed with PEG-OH had very close yields. The presence of PEG-OH does not seem to significantly affect the course of the polymerization.

The polymerization in the presence of the macroRAFT agent achieved the lowest yield. However, this was the polymerization (RL-PE 09) that had the highest yield from the polymerizations performed with PEG-X. Indeed, the first experiments of this type involved a larger amount of PEG-X in the initial solution, and lead to a very low yield (almost no PE formed). This can be possibly explained by the initial molar ratio of PEG-X/AIBA, which would not be in the optimal range for obtaining the maximum yield (PEG-X/AIBA=0.6).

The influence of the PEG-X/AIBA ratio will be discussed below.

Comparison of the particle morphology for the different types of polymerization

The morphology of the PE particles in the latexes was analysed by Transmission Electron Microscopy (TEM), which allowed to evaluate particle size. The TEM pictures that characterize each type of latex are presented in Figure 7.

The TEM pictures support the conclusions drawn out from visual aspect with the resemblance between two groups of polymerizations (blank and PEG-OH versus CTAB and PEG-X).

The Blank experiments yielded relatively large spherical particles, 75 nm, (Figure 7-[1]), similarly to the polymerization carried out in the presence of PEG-OH (Figure 7-[3]).

The polymerizations carried out with CTAB (Figure 7-[2]) or with PEG-X (Figure 7-[4]) originated a main population of particles with a diameter around 25 nm. The particles appeared to be non-spherical or disk-like shaped these unusual kinds of structures were attributed to the crystallinity of the polymer that seemed to prevent the formation of spherical particles.^[9] Indeed, morphologies different from the spherical one can be obtained in the frame of the PISA process.^[18]

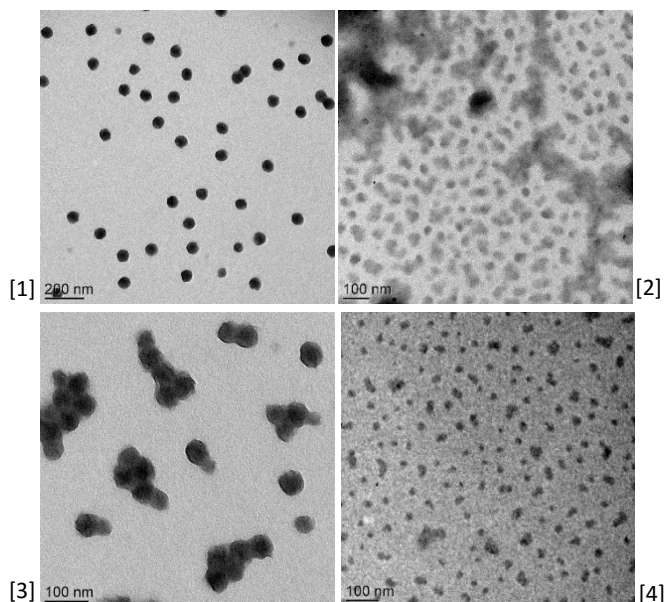


Figure 7 - TEM of PE particles: [1] – Blank; [2] – CTAB; [3] – PEG-OH; [4] – PEG-X.

Comparison of the Dynamic Light Scattering data

The four latexes were analysed by DLS, providing the hydrodynamic particle size, Z_{av} , and the polydispersity index (PDI), which usually gives an indication of the “homogeneity” of particle size distribution. Again the polymerizations can be divided into two groups.

The “large particle size group” concerns the latexes obtained from the polymerizations without surfactant or with PEG-OH that yielded the same particle size, around 75 nm and had a very low PDI value (0.02) reflecting a monomodal particle size distribution. This corroborated the results from TEM and was another indicator of the resemblance between these two polymerizations and the lack of influence by the PEG backbone on the ethylene polymerization. The particle morphology was spherical.

In the “small particle size group” are present the polymerization performed with the PEG-X and the one performed with CTAB. As observed by TEM, the first yielded a main population with the particle size around 25 nm with high PDI (0.25), which was interpreted as a deviation from the spherical morphology and the inadequacy of the DLS measurements in this case. The presence of bigger objects was observed, in agreement with TEM. Based on the theory associated with DLS it was assumed that the number of the smaller particles surpassed greatly the number of the particles from the larger size population, having a signal much more intense (proportional to radius of the particle - $\approx r^6$).

The polymerization performed with CTAB yielded a two particle population. The population of small particle size ≈ 25 nm was predominant because the intensity of this population ($\approx 64\%$) surpasses greatly the one of the population with large particles ($\approx 36\%$), turning these results comparable with those for the polymerization with the macroRAFT. The large objects in this sample may be large PE particles, but also objects formed of CTAB, such as vesicles, as previously reported.^[21]

Table 2 - Particle sizes and PDI of the four polymerizations. (4h, 50 mg AIBA, T=70°C, and $P_{ethylene} \approx 100$ bar).

Polymerization Type	Name of sample	Quantity ⁽¹⁾	Z_{av} (nm) [PDI]
Polyethylene Glycol Xanthate (PEG-X)	RL-PE 09	0.3	20 [0.249]
With surfactant (CTAB)	RL-PE 20	50 mg	25/865 ⁽²⁾
Without surfactant (Blank)	RL-PE 18	--	75 [0.02]
Poly(ethylene glycol) (PEG-OH)	RL-PE 14	1 g	72 [0.02]

⁽¹⁾ – mass introduced in the initial solution (CTAB, PEG-OH, PEG-X);

⁽²⁾ -Two particle populations.

Comparison of Differential Scanning Calorimetry (DSC) data

The samples obtained from the four different types of polymerization were analysed by DSC and the melting and crystallization temperatures (T_m and T_c) and crystallinity from crystallization and melting curves (X_c and X_m) were determined (Table 3).

Table 3 -Comparison of DSC values for the different types of polymerizations (4h, 50 mg AIBA, 70°C, and $P_{\text{ethylene}} \approx 100$ bar).

Polymerization Type	Name of sample	T_m (°C)	T_c (°C)	X_c (%)	X_m (%)
Without surfactant (Blank)	RL-PE 18	96	76	16	10
With surfactant (CTAB)	RL-PE 20	93	72	26	16
Poly(ethylene glycol) (PEG-OH)	RL-PE 14	52/96	24/79	21/6	27/3
Polyethylene Glycol Xanthate (PEG-X)	RL-PE 09	96	81	16	12

The blank experiments yielded a PE, with low crystallinity, lower than in previous studies (23%) but the T_m was in agreement for the same system (93°C). However, lower than the usual T_m of commercial LDPE ($\approx 100^\circ\text{C}$). The polymerization with CTAB was more consistent with the previous studies, the crystallinity and T_m were in-line with other studies (23% and 93°C, respectively).^[21]

The DSC analysis of the product from the polymerization with PEG-OH revealed two peaks in each curve (Figure 8). This situation was interpreted as the existence of two different polymer species in the sample, possibly one related to the poly(ethylene glycol) and the other to polyethylene, with the melting temperatures (52°C^[20] and 95°C, respectively) near the ones reported for each.

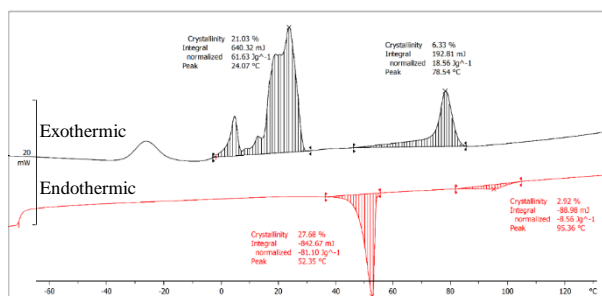


Figure 8 -DSC analyses of RL-PE 14 sample (1 g PEG-OH, 4h, 50 mg AIBA, 250 rpm, T=70°C, and $P_{\text{ethylene}} \approx 100$ bar).

The DSC analysis of the product isolated from the polymerization carried out with PEG-X showed a very broad peak both on melting and crystallization curves. The existence of just one broad signal can be an indicator that the PEG-X is not free anymore, but trapped in a block copolymer structure.

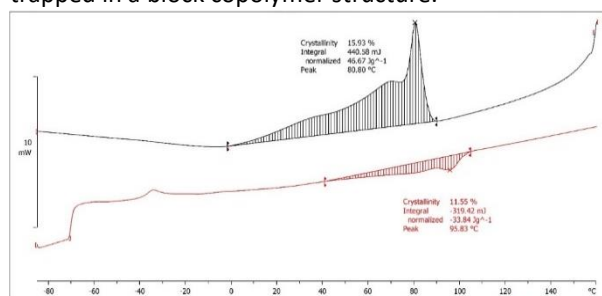


Figure 9 -DSC analyses of RL-PE 09 sample (0.3 g PEG-X, 4h, 50 mg AIBA, 250 rpm, T=70°C, and $P_{\text{ethylene}} \approx 100$ bar).

Comparison between polymer molar masses

The M_n and dispersity values are gathered in the next table.

Table 4 - M_n and \mathcal{D} for the different types of polymerizations (4h, 50 mg AIBA, 250 rpm, T=70°C, and $P_{\text{ethylene}} \approx 100$ bar).

Polymerization Type	Name of sample	M_n (g mol^{-1})	Dispersity (\mathcal{D})
Polyethylene Glycol Xanthate (PEG-X)	RL-PE 09	2800	8.6
Without surfactant (Blank)	RL-PE 18	2700	5.1
Poly(ethylene glycol) (PEG-OH)	RL-PE 14	2800	5.6
With surfactant (CTAB)	RL-PE 20	5000/ $2,7 \times 10^5$	5.6/1.2

The values for the blank experiment and the polymerization with PEG-OH are similar. Such proximity can be explained by the low effect that PEG-OH has on the behaviour of the polymerization. In practical terms the polymerization is mainly dictated by the presence of the initiator, which ensures the stabilization of the systems with positively charged fragments at the chain-ends (even if PEG-OH may participate to the stabilization due to transfer reactions on its backbone, leading to the formation of a graft polymer which can be anchored onto the particle surface). Both blank and PEG-OH samples have dispersities around 5 that might be related to the poor of control in these systems.

The product obtained from the polymerization in the presence of PEG-X presented a rather low M_n , in the same range of the first two cases. Although the dispersity is broader (8.6), likely related to the poor of control in these systems.

The polymerization with surfactant was intrinsically different from the other. From previous studies was expected that it would give rise to two different molar mass populations, one with low M_n and another with very high M_n , which indeed happened (Table 4).

Effect of the macroRAFT amount on polymerization

The first polymerizations with PEG-X revealed that the obtained PE yield was strongly related to the quantity of macroRAFT agent, being almost inhibited in some cases (PEG-X/AIBA=2.3). Hence, a study to evaluate the effect of PEG-X amount on the resulting latexes was carried on. A set of polymerizations were performed maintaining the same reaction conditions, while quantity of PEG-X (≈ 1 g, 0.5 g and 0.3 g) and the PEG-X/AIBA ratio were varied. The recovered latexes were all stable and translucent.

As the quantity of PEG-X decreased, the polymer content of the samples increased significantly. However, the particle size and correspondent PDI values remained in the same range for the different quantities of PEG-X as seen below.

Table 5 -Yields, Z_{av} and PDI of the polymerizations performed with PEG-X. ([1 g, 0.5 and 0.3 g of PEG-X], 4h, 50 mg AIBA, $T=70^{\circ}\text{C}$, and $P_{\text{ethylene}}\approx 100$ bar).

Name of sample	PEG-X (g)	Molar ratio (PEG-X/AIBA)	Yield (g) / PC (%)	Z_{av} (nm) [PDI]
RL-PE 07	1	2.3	0.1 (0.2)	25[0.272]
RL-PE 08	0.5	1.2	0.3 (0.6)	19[0.189]
RL-PE 09	0.3	0.6	0.5 (0.9)	20[0.249]

DSC analysis of the experiment carried out with 1 g of PEG-X (RL-PE 07, PEG-X/AIBA=2.3) revealed that there was almost no polyethylene in that sample. The obtained T_m , T_c and crystallinity values are close to the ones obtained in the DSC analysis of PEG-X.

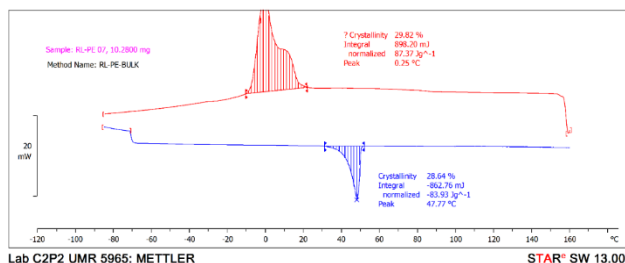


Figure 10 -DSC analyses of RL-PE 07 sample (1 g PEG-X, 4h, 50 mg AIBA, 250 rpm, $T=70^{\circ}\text{C}$, and $P_{\text{ethylene}}\approx 100$ bar).

The molar mass increases slightly as the quantity of PEG-X decreases in the system (from RL-PE 07 to RL-PE 09). Also, the broadness of the molar mass distribution seemed to be larger (Table 6).

Table 6 - M_n and \mathcal{D} (RL-PE 07;08; RL-PE 09) ([1 g, 0.5 and 0.3 g of PEG-X], 4h, 50 mg AIBA, $T=70^{\circ}\text{C}$, and $P_{\text{ethylene}}\approx 100$ bar).

Name of sample	PEG-X (g)	M_n (g mol^{-1})	\mathcal{D}
RL-PE 07	1	≈ 2600	1.9
RL-PE 08	0.5	≈ 2800	4.4
RL-PE 09	0.3	≈ 2800	8.6

Kinetic study on the polymerization of ethylene in the presence of PEG-X

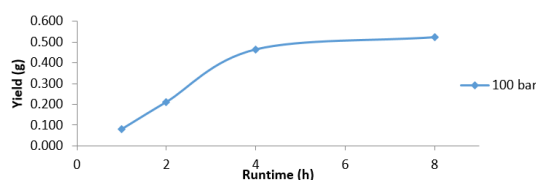
In order to perform a kinetic study, several polymerizations were carried in the same reaction conditions, maintaining the same amount of PEG-X (0.3 g). As withdrawal of samples at high pressure were not possible, identical reactions at different polymerization durations (1, 2, 4 and 8 hours) were performed. This study was performed at two different pressures, 100 and 200 bar.

Whatever the reaction duration the recovered latexes from the polymerizations carried out at 100 bar, were stable and had a translucent aspect as seen in Figure 14-[1]. The latexes recovered at 200 bar were noticeably less stable than the ones at 100 bar. The experiments performed for the shortest times (1 and 2 hours) yielded latexes with a translucent appearance Figure 14-[2]. However, the polymerizations with a duration of 4 and 8 hours seem to exhibit larger particle sizes (milky aspect) and some coagulum on the walls of the sample flask was observed (Figure 14-[3]). These observations were confirmed by the values of particle size and particle size distribution later obtained DLS.



Figure 14 -Polymerization sample of FREPE ([1] -1h, 100 bar); ([2] -2h, 200 bar); ([3] -8h, 200 bar) (50 mg AIBA, 0.3 g PEG-X, 250 rpm, $T=70^{\circ}\text{C}$).

At 100 bar, the yield increased with the polymerization time. However, from 4 hours on the yield on polyethylene seemed to attain a plateau. This evolution is present in the following figure.



Similarly to the polymerizations at 100 bar, the

Figure 11 -Yield as function of time in FREPE with PEG-X. (1h, 2h, 4h, 8h) (100 bar, 50 mg AIBA, 0.3 g PEG-X, $T=70^{\circ}\text{C}$).

yield increased along the polymerization time at 200 bar. In this case, the overall yield was higher than the latter for the same polymerization time. The yield increased from the first hour to the polymerization time of 4 hours, at almost the same rate as the procedures at 100 bar, doubling between experiments (from 1h to 2h and from 2h to 4h). However, instead of plateauing, the yield almost tripled between 4h and 8h but some coagulation occurred in the latter case.

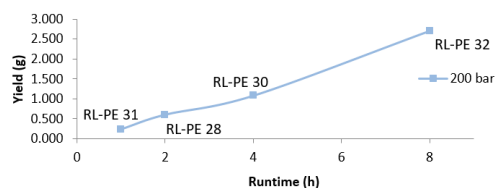


Figure 12 - Yield vs. polymerization time in FREPE using PEG-X (1h, 2h, 4h, 8h) (200 bar, 50 mg AIBA, 0.3 g PEG-X, $T=70^{\circ}\text{C}$).

TEM analysis was performed for the sample RL-PE 27 (8 h). Very small particles were consistently observed in the 20 nm range, which seem to have a disk-like morphology. In the TEM picture of the sample RL-PE 28 (2 h) is possible to observe the presence of a very large number of small non-spherical particles and also the presence of larger particles.

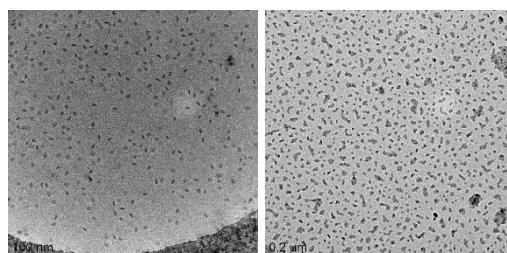


Figure 13 -TEM (8 h, 100 bar); (right) (2h, 200 bar) (50 mg AIBA, 0.3 g PEG-X, 250 rpm, $T=70^{\circ}\text{C}$).

At 100 bar the polymerization with a duration of 1h had two populations of particles present. A smaller particle population with ($Z_{av} \approx 19$ nm) and a larger one ($Z_{av} \approx 83$ nm), which had the higher intensity signal (65%). After two hours of polymerization the population with higher particle size was practically not detected by DLS. A similar phenomenon was previously reported by *E. Grau* during the kinetic study of the polymerization performed with surfactant, which was explained by shattering of the larger particles into smaller ones under heating and the presence of CTAB.^[9] However, in his work on the same system, *G. Billuart* stated that probably the extinction of the larger particles population did not take place. Instead, it was shown that the former DLS apparatus was not efficient in detecting the two populations. Based on the theory associated with DLS it was assumed that the number of the smaller particles surpassed greatly the number of the particles from the larger size population, having a signal much more intense. Although the interpretation of these phenomena is not trivial, this might be a possible explanation for this system.

At 200 bar the population with lower particle sizes represented majority of the intensity signal. However, a second population of large particle size was systematically observed.

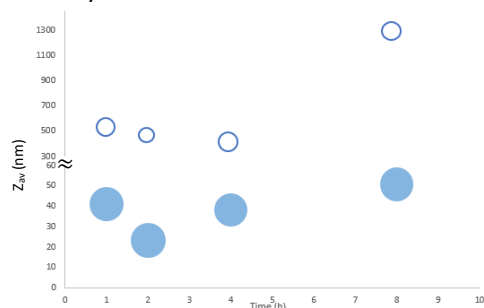


Figure 15 - Particle size as a function of time (circle proportional to the intensity signal) in FREPE (RL-PE 31, 1h), (RL-PE 28, 2h), (RL-PE 30, 4h), (RL-PE 32, 8h) (200 bar, 50 mg AIBA, 0.3 g PEG-X, T=70°C).

For both polymerization pressures, the molar masses increased with time and very high dispersities were observed (Table 7).

Table 7 - M_n and \mathcal{D} of FREPE of ethylene at 100 and 200 bar and with PEG-X (50 mg AIBA, 0.3 g PEG-X, 250 rpm, T=70°C).

Run	Time (h)	Pressure (bar)	M_n (g mol ⁻¹)	Dispersity (\mathcal{D})
RL-PE 26	1	100	2500	4.0
RL-PE 29	2		2700	2.3
RL-PE 09	4		2800	8.6
RL-PE 27	8		2800	5.8
RL-PE 31	1	200	3100	8.7
RL-PE 28	2		4400	8.7
RL-PE 30	4		5100	13.0
RL-PE 32	8		7200	17.6

Conclusions

The aim of the work was the implementation of the RAFT polymerization of ethylene in a surfactant-free emulsion process to obtain, from water-soluble functional polymers, aqueous dispersions of PE-based

nanoparticles by the PISA process, relying on the knowledge developed at the C2P2, on the possibility of performing FREPE under mild conditions ($T < 100^\circ\text{C}$ and $P < 250$ bar) and the CRP of ethylene via RAFT. In addition, the concepts developed at C2P2 for the synthesis of block copolymers produced by emulsion polymerization according to the PISA process were also considered, and relied on the chain extension of a preformed hydrophilic polymer produced by RAFT by a hydrophobic monomer in water.

The FREPE required benchmarks experiments. Thus, a set of four different reactions was performed in order to evaluate the activity of the xanthate chain-end.

In terms of visual aspect it was possible to set two groups of latexes: the polymerization carried out only with AIBA and in the presence of PEG-OH yielded a stable and milky white latex. This suggested the presence of relatively large size particles (≈ 100 nm). On the other hand, a stable translucent latex was synthesized either in the presence of surfactant (CTAB) or in the process with PEG-X. The translucent aspect suggested the presence of small size particles (≈ 25 nm) in the latexes.

Indeed, TEM pictures showed that the polymerization performed only with initiator and the one in the presence of PEG-OH had relatively large spherical particles (≈ 75 nm). The similarity between the two experiments would indicate that PEG-OH had no influence in the polymerization of ethylene. For the polymerizations carried out with surfactant and the ones performed with PEG-X it was observed a vast majority of small size particles (≈ 25 nm). The morphology of the particles from the latexes obtained in the presence of CTAB was disk-like shaped. In the case of the polymerization with PEG-X, other morphologies were observed such as cylindrical shapes. These unusual kinds of structures can be of obtained by the PISA process. The crystallinity may favour the formation of such non-spherical particles. The aspect of the latexes and the TEM pictures revealed a striking difference between the polymerization performed in the presence of PEG-OH and PEG-X. DLS analysis supported TEM observations.

The polymerization only with initiator and the one in presence of PEG-OH had the same yield, supporting the conclusions drawn above on the role of PEG-OH. The lowest yield was obtained for the polymerization in presence of the PEG-X.

DSC analyses of the product from the polymerization in the presence of PEG-OH, two peaks were observed, which was correlated with the presence of two polymer species in the sample, probably PEG-OH and PE. The DSC of the product obtained from the polymerization with PEG-X revealed a broad signal with no evidence of isolated PEG-X, which could be interpreted as the formation of a block copolymer structure, together with PE homopolymer.

The main conclusions brought by these analyses are the following: The presence of PEG-OH did not influence the process of polymerization. The polymerizations performed with PEG-X showed different behaviour, indicating that the xanthate-functionalized PEG chains participated to the free radical process.

This study also showed that the amount of PEG-X in the system has a great effect on the yield obtained - As the quantity of PEG-X increased the yield decreased. On the other hand, it had no or little effect on the particle size or on the molar masses.

The kinetic study was performed at two different pressures, 100 and 200 bar. At 100 bar, the recovered latexes were stable and had a translucent aspect. However, after 1 hour of polymerization two particle populations were observed. After two hours they were no longer observed. This phenomenon was mainly attributed to the outnumbering of the larger particles population by the smaller ones ($Z_{av} \approx 20$ nm).

At 200 bar the recovered latexes were stable at short polymerization times (1 and 2 hours) and had a translucent aspect. After 4 h, the latexes appeared to be less stable, having a milky aspect and some coagula were observable. The molar mass increased linearly with the polymerization yield, which again could be an indicator of some livingness of the polymerization.

With all the acquired data it is possible to conclude that indeed, the aim of this project was achieved. The emulsion polymerization of ethylene mediated by a xanthate macroRAFT can lead to the formation of PE-based nanoparticles by a PISA process. The block copolymers formed in situ would provide the stabilization of particles.

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