

## 2-oxazoline telechelic polymers: Synthesis and characterization

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**Abstract:** New telechelic polymers functionalized with terminal ethyl xanthate or vinyl groups were synthesized via cationic ring-opening polymerization (CROP). The polymerization of 2-ethyl-2-oxazoline (Etoxa) and 2-methoxycarbonylethyl-2-oxazoline (Esteroxa) was initiated by 1,4-trans-dibromobutene in acetonitrile at 78 °C, with termination using either potassium ethyl xanthate or 4-vinylbenzyl-piperazine. Structural characterization by <sup>1</sup>H and <sup>13</sup>C NMR and FTIR spectroscopy confirmed the telechelic architecture. <sup>1</sup>H NMR analysis revealed degrees of polymerization (DP) of 24–29 for ethyl xanthate-terminated polymers and 22–23 for vinyl-terminated polymers, consistent with theoretical values. The molar compositions of Etoxa and Esteroxa in all telechelic polymers matched the initial monomer feed ratios. End-group functionalization efficiency was quantified as follows: Ethyl xanthate-terminated polymers: 64%–82%, and vinyl-terminated polymers: 69% and 98% (for respective batches).

**Keywords:** 2-oxazolines; telechelic polymer; cationic polymerization

## 1. Introduction

2-Oxazolines are monomers that polymerize via cationic ring-opening polymerization, producing linear polymers [1,2]. Initiators for this polymerization include, for example, methyl tosylate and methyl triflate, among others [1]. The most important characteristic of this polymerization is that it proceeds in a “living” manner, meaning without side reactions such as termination or chain transfer reactions. Therefore, polymers with predetermined degrees of polymerization and functionalization can be obtained [3–5]. The polymerization of 2-oxazolines enables the preparation of polymer architectures such as, for example, telechelic polymers, macromonomers, block copolymers, graft copolymers, hydrogels, etc. [1–7].

Telechelic polymers are polymers containing chemical functional groups at both chain ends. These chemical functions can be, for example, amines, carboxylic acids, vinyl groups, etc. [3]. These polymers can be synthesized, for instance, via the termination method, where the chemical function is introduced through the reaction of the terminating agent with the propagating chain. Telechelic polymers serve to synthesize various polymers such as hydrogels, lipogels, cyclic polymers, etc. [1,3]. The United States Food and Drug Administration (FDA) considers poly(methyloxazoline) and poly(ethyloxazoline) to be biocompatible polymers, and for this reason, there is significant interest among research groups worldwide in these types of polymers for applications in the field of medicine [2].

This study presents the synthesis and characterization of telechelic polyoxazoline polymers functionalized with ethyl xanthate and vinyl groups at the polymer chain ends.

## 2. Materials and methods

The substances used in this research were employed as received or were purified and dried according to standard methods described in the literature [6–10]. Methyl succinyl chloride (purity: 97%, source: Aldrich), 2-chloroethylamine hydrochloride (97%, Merck), triethylamine (98%, Merck), 2-ethyl-2-oxazoline (97%, Merck) was distilled before use, 4-vinylbenzyl chloride (97%, Aldrich) distilled, and piperazine (97%, Aldrich). Nuclear magnetic resonance (NMR), Fourier-transform infrared (FTIR), ultraviolet/visible (UV/Vis) spectroscopy, and gel permeation chromatography (GPC) analyses of substances used or generated in this research were performed using standard methods from the literature [6–8].

Gel Permeation Chromatography (GPC), Waters System with IR 410 and UV 486 detectors; Columns: Ultrastaygel™ (7 μm particle size), pore sizes: 500, 10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup> Angstrom. Bruker Advance III 500 NMR nuclear magnetic resonance (NMR) spectrometer, 500.13 MHz for <sup>1</sup>H and 125.75 MHz for <sup>13</sup>C, deuterated chloroform solvent. Fourier-Transform Infrared (FTIR) Spectroscopy PerkinElmer Spectrum 100 with ATR accessory. Thermoelectron Corporation Helios Gamma UV-Visible Spectrometer.

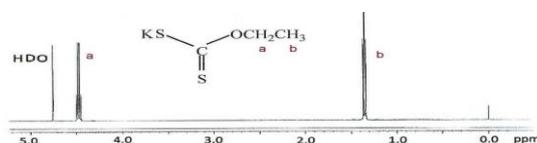
### 2.1. Purification of the initiator trans-1,4-dibromobutene (DBB)

4.11 g of DBB was added to a 100 mL beaker, followed by the addition of 10 mL of hexane. The mixture was heated to 70 °C until complete dissolution was achieved. Stirring was discontinued, and the solution was cooled to room temperature. The formation of white DBB crystals was observed. The crystals were filtered and redissolved in hexane (10 mL) at 70 °C. The solution was again cooled, yielding DBB crystals once more. The purified DBB was dried and stored at low temperature (5 °C) in a nitrogen-purged, hermetically sealed flask.

<sup>1</sup>H-RMN (CDCl<sub>3</sub>) δ: 3.95 (–CH<sub>2</sub>–Br); 5.98 (H–C=C).

### 2.2. Purification of potassium ethyl xanthate

Potassium ethyl xanthate was purified through recrystallizations in toluene and heptane [11]. 9.3 g of potassium ethyl xanthate was dissolved in 200 mL of acetone at 40 °C. The solution was filtered and concentrated by evaporation. 800 mL of distilled, dry toluene was slowly added to the solution. Precipitation of potassium ethyl xanthate was observed. The supernatant solvent was removed and dried under a stream of dry nitrogen. The procedure was repeated using hexane as the precipitating medium. Finally, the potassium ethyl xanthate was stored in the dark and at low temperature (5 °C). The mass loss during the purification process was 30%. Its structure was confirmed by nuclear magnetic resonance (**Figure 1**). <sup>1</sup>H-RMN (D<sub>2</sub>O) δ: 1.35 (CH<sub>3</sub>, triplet); 4.45 (CH<sub>2</sub>-O, quadruplet), 4.75 (HDO).



**Figure 1.** <sup>1</sup>H NMR spectrum of potassium ethyl xanthate in deuterated water at 25 °C.

### 2.3. Determination of the purity of potassium ethyl xanthate using ultraviolet/visible spectrometry [11]

0.069 g of purified potassium ethyl xanthate was weighed into a 100 mL beaker and dissolved in 50 mL of distilled water. This solution was transferred to a 100 mL volumetric flask and diluted to the mark with pure water. An 8.8 mL aliquot was taken and transferred to a 500 mL volumetric flask, then diluted to the mark with distilled water. Finally, the maximum absorbance of this aqueous potassium ethyl xanthate solution was measured at 226 nm and 302 nm using UV/vis spectrophotometry. The ratio of the absorbance peak at 226 nm to that at 302 nm was 0.50, consistent with literature values [10]. The absorbance at 302 nm was used to determine the extinction coefficient ( $\epsilon$ ) of this compound, yielding a value of 17,350. This aligns with the literature-reported value for pure potassium ethyl xanthate (17,500) [11]. Therefore, based on the UV and NMR results, the potassium ethyl xanthate was estimated to be of high purity.

### 2.4. Synthesis of 2-methoxycarbonylethyl-2-oxazoline (Esteroxa) [6,9]

First, methyl 7-chloro-4-oxo-5-azaheptanoate was synthesized by the reaction, in 150 mL of dichloromethane, of methyl succinyl chloride (20 g) and 2-chloroethylammonium hydrochloride (15.4 g) in the presence of triethylamine (30 g) at 0 °C. A yield of 74% was obtained. Then, in a second step, 2-methoxycarbonylethyl-2-oxazoline (Esteroxa) was obtained from the cyclization of 19 g. Methyl 7-chloro-4-oxo-5-azaheptanoate with 7.6 g of anhydrous sodium carbonate and the application of vacuum (0.5 mmHg) for 60 min [5,6,8]. The yield was 60%. Esteroxa was characterized by NMR:  $^1\text{H-RMN}$  ( $\text{CDCl}_3$ )  $\delta$ : 2.44 ( $-\text{CH}_2\text{CH}_2\text{CO}-$ ); 2.58 ( $\text{CH}_2-\text{CO}$ ); 3.67 ( $\text{CH}_3\text{OCO}$ ); 3.71 ( $\text{CH}_2-\text{N}=\text{}$ ); 4.17 ( $\text{CH}_2-\text{O}$ ).  $^{13}\text{C-RMN}$  ( $\text{CDCl}_3$ )  $\delta$ : 22.5 ( $-\text{CH}_2\text{CH}_2\text{CO}-$ ); 29.6 ( $-\text{CH}_2\text{CH}_2\text{CO}$ ); 51.4 ( $\text{CH}_3\text{OCO}$ ); 53.8 ( $\text{CH}_2-\text{N}=\text{C}$ ); 66.9 ( $\text{CH}_2-\text{O}-\text{C}$ ); 165.9 ( $\text{N}=\text{C}-\text{O}$ ); 172.3 ( $\text{O}-\text{C}=\text{O}$ ).

### 2.5. Synthesis of 4-vinylbenzylpiperazine (4-VBP) [12]

The synthesis of 4-VBP is described in the literature by Gross et al. [12]. This synthesis consists of reacting vinylbenzyl chloride at 0 °C with a large molar excess (15/1) of anhydrous piperazine in anhydrous chloroform. A reddish-yellow liquid was obtained with a 95% yield.

$^1\text{H-RMN}$  (and  $\text{CDCl}_3$ )  $\delta$ : 1.51 (NH); 2.40 ( $\text{NCH}_2-$ ); 2.83 ( $\text{CH}_2-\text{NH}$ ); 3.46 ( $\text{Ar}-\text{CH}_2$ ); 5.2; 5.7, 6.7 ( $\text{CH}_2-\text{CH}-$ ); 7.3 (Har).

### 2.6. Synthesis of telechelic polymers with ethyl xanthate terminal groups

First, the polymerization of the monomers 2-ethyl-2-oxazoline (Etoxa) and 2-methoxycarbonylethyl-2-oxazoline (Esteroxa) (in a molar ratio of Etoxa/Esteroxa = 80/20) was carried out via a cationic ring-opening polymerization initiated by 1,4-trans-dibromobutene (DBB) in acetonitrile at 78 °C in a reaction time of 5.5 h, and it was determined that in this reaction time 100% conversion of the monomers was reached. Secondly, all other experiments were performed using this reaction time and under the same reaction conditions. Typical example: (Polymer P1): 0.5 g (2.33 mmol) of DBB, 4.12 g (41.6 mmol) of Etoxa, 1.62 g (10.3 mmol) of Esteroxa, and 12.5 mL

of acetonitrile were placed in a reactor under a dry nitrogen atmosphere. It was polymerized at 78 °C and after 5.5 h the reaction mixture was cooled to room temperature and the polymerization was terminated with 3.7 g (23.3 mmol) of potassium ethyl xanthate dissolved in 50 mL of acetonitrile. The reaction mixture was filtered, and the solvent was evaporated at atmospheric pressure. Then, 40 mL of dichloromethane was added (to decrease the viscosity of the mixture), and it was washed three times with 25 mL of a saturated sodium chloride solution (to remove the remaining potassium ethyl xanthate salt). Finally, 4 g of MgSO<sub>4</sub> was added to the mixture to dry the solution. The mixture was then filtered, and the solvent was evaporated, obtaining a polymer. The polymer was dissolved in 20 mL of chloroform and precipitated in 200 mL of diethyl ether. This process (dissolution-precipitation) was repeated three times, and finally the dry polymer was stored in a hermetically sealed vial at 5 °C, under a dry nitrogen atmosphere. This polymer was characterized by NMR and FTIR: <sup>1</sup>H-RMN (CDCl<sub>3</sub>) δ: 1.12 (–CH<sub>3</sub>); 1.42 (CH<sub>3</sub>–CH<sub>2</sub>–OC=S); 2.39 (–CO–CH<sub>2</sub>–CH<sub>3</sub>); 2.65 (–CH<sub>2</sub>CH<sub>2</sub>–CO–O); 3.45 (N–CH<sub>2</sub>); 3.65 (O–CH<sub>3</sub>); 3.95 (=CHCH<sub>2</sub>); 4.65 (O–CH<sub>2</sub>–CH<sub>3</sub>); 5.53 (=CH–).

<sup>13</sup>C-RMN (CDCl<sub>3</sub>) δ: 174.5 (C=O); 127.5 (C=C); 70.6 (S–COCH<sub>2</sub>); 51.7 (OCH<sub>3</sub>); 50.0 (=CH–CH<sub>2</sub>); 45.3 (NCH<sub>2</sub>CH<sub>2</sub>); 33.6 (–CH<sub>2</sub>SC); 25.9 (COCH<sub>2</sub>CH<sub>3</sub>); 13.7(–CSO–CH<sub>2</sub>CH<sub>3</sub>), 9.3 (COCH<sub>2</sub>CH<sub>3</sub>). FTIR (cm<sup>–1</sup>): 2.978 (C–H aliphatic), 1.734 (C=O, ester), 1.629 (N–C=O amide), 1.193 (C=S) [13].

In the case of the telechelic finished with vinyl groups, the procedure was similar, except that at the time of finishing, 2.82 g were added. 4-vinylbenzylpiperazine (in the case of PB polymers) was added to the reaction mixture. To deprotonate the end of the polymer chain, the mixture was stirred with potassium carbonate at 20 °C for 12 h. It was filtered and precipitated in diethyl ether three times. It was characterized via NMR:

<sup>1</sup>H-RMN (CDCl<sub>3</sub>) δ: 1.10 (–CH<sub>3</sub>); 2.30 (–CO–CH<sub>2</sub>–CH<sub>3</sub>); 2.65 (–CH<sub>2</sub>CH<sub>2</sub>–COO); 3.40 (N–CH<sub>2</sub>); 3.65 (O–CH<sub>3</sub>); 3.95 (=CHCH<sub>2</sub>); 5.3, 5.7 (CH<sub>2</sub>–CH); 5.5 (=CHCH<sub>2</sub>); 6.7 (=CH–), 7.2–7.6 (Har).

## 2.7. Cyclization of the telechelic polymer containing ethylxanthate functions

Typical procedure: In a glass flask, 2.0 g of polymer P1 and 0.7583 g (10.4 mmol) of n-butylamine were dissolved in 500 mL of tetrahydrofuran (THF), which was previously dried with metallic sodium and distilled. Air was bubbled into the glass jar using a bulb and a pipette for 24 h. After this period, the tetrahydrofuran was removed by evaporation until the dry polymer was obtained. The polymer was dissolved in chloroform and precipitated in diethyl ether. The resulting polymer was filtered and dried. The polymer was stored in a hermetically sealed vial and named P1-S-S. This polymer was characterized by NMR.

<sup>1</sup>H-RMN (CDCl<sub>3</sub>) δ: 1.13 (–CH<sub>3</sub>); 2.39 (–CO–CH<sub>2</sub>–CH<sub>3</sub>); 2.6 (–CH<sub>2</sub>–CO–O); 2.85 (–CH<sub>2</sub>–S–S–CH<sub>2</sub>–); 3.45 (N–CH<sub>2</sub>–CH<sub>2</sub>–N); 3.65 (O–CH<sub>3</sub>); 3.95 (=CHCH<sub>2</sub>); 5.53 (=CH–).

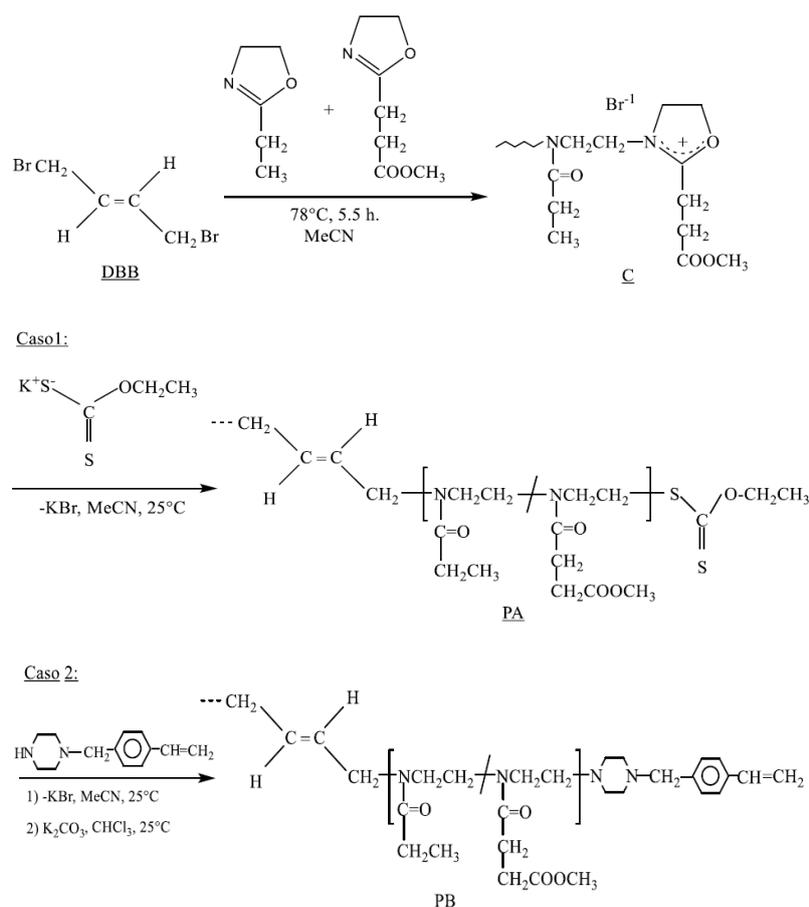
### 3. Results and discussion

The monomers 2-ethyl-2-oxazoline (Etoxa) and 2-methoxycarbonylethyl-2-oxazoline (Esteroxa) were polymerized via a cationic ring-opening polymerization initiated by 1,4-*trans*-dibromobutene (DBB). In all experiments, a reaction time of 5.5 h at 78 °C was always used because in this reaction time, and under the same reaction conditions, 100% conversion of the monomers was reached. The molar percentage of Esteroxa was varied between 18% and 44% so that in further investigation, the ester groups could be hydrolyzed and carboxylic acid groups obtained, which could make it possible to introduce new functionalities and properties to the telechelic polymers. The initiator 1,4-*trans*-dibromobutene (DBB) is a dual-functional initiator, and therefore two polymer chains are initiated per molecule of DBB initiator.

#### 3.1. Synthesis and characterization of telechelic polymers with ethyl xanthate terminal groups

The telechelics of Etoxa and Esteroxa with ethyl xanthate groups were obtained by terminating the polymerization with a solution of potassium ethylxanthate in acetonitrile (Scheme 1, case 1). At the end of the polymerization with potassium ethyl xanthate, this functional group was introduced at the two ends of the polymer chain, thus forming a telechelic polymer. **Table 1** (PA Polymers) shows the polymerization conditions and the results obtained. The structure of the telechelic polymers was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectra (e.g., <sup>1</sup>H NMR spectra of PA2 and <sup>13</sup>C NMR spectra of PA1 in **Figures 2** and **3**, respectively).

The molar percentages of the Etoxa and Esteroxa monomers in the telechelic copolymers were found by quantitative analysis of the <sup>1</sup>H NMR spectrum (**Figure 2**), comparing the signals “f” (of Etoxa) versus “h+i” (of Esteroxa), and this ratio was similar to the initial molar ratio of these monomers (**Table 1**). The degree of polymerization of the telechelic polymers was found by comparing the sum of the signals “f” and “h+i” versus the initiator signal “a” and was very close to the value of the initial molar ratio (Etoxa+EsterOxa)/Initiator) (**Table 1**). This was evidence that the polymerization occurred in a “live” manner, that is, only the initiation and propagation reactions occurred and not the secondary reactions such as chain transfer or termination reactions. Functionalization with ethyl xanthate groups was determined by comparing the integrals of the signals “c” and “a”. However, the percentages of functionalization with ethyl xanthate were not greater than 82% despite the use of a large molar excess (10 to 1) of potassium ethyl xanthate in the termination reaction to statistically force the inclusion of this substance at the chain end. This result means that some ends of the polymer chains of the telechelic polymers did not contain the ethyl xanthate group. It is likely that termination would have occurred by reaction of the propagating oxazoline chains with traces of moisture in some component of the reaction system or that, as postulated later, a part of the ethyl xanthate group incorporated into the polymer was lost in the purification process by secondary reactions. So, as a result, a mixture of polymers was obtained, some (higher percentage) containing two ethyl xanthate groups at both ends (telechelic polymers) and a small percentage of the polymers with a single ethyl xanthate group at their chain ends.

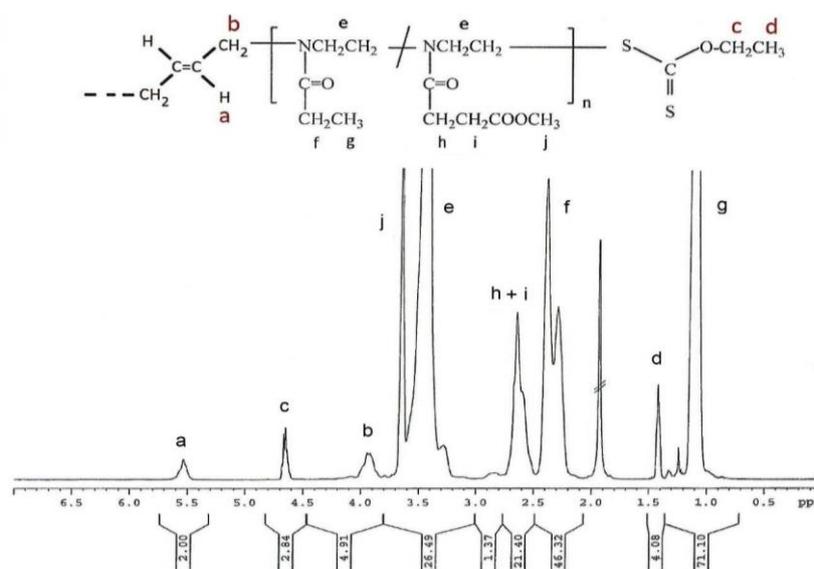


**Scheme 1.** Reaction mechanism for the synthesis of telechelic polymers with ethyl xanthate and vinyl end groups. DBB (initiator) = 1,4-*trans*-Dibromobutene, C=propagating oxazolinone cation. Case 1 and Case 2: termination reactions with potassium ethyl xanthate and 4-vinylbenzylpiperazine, respectively.

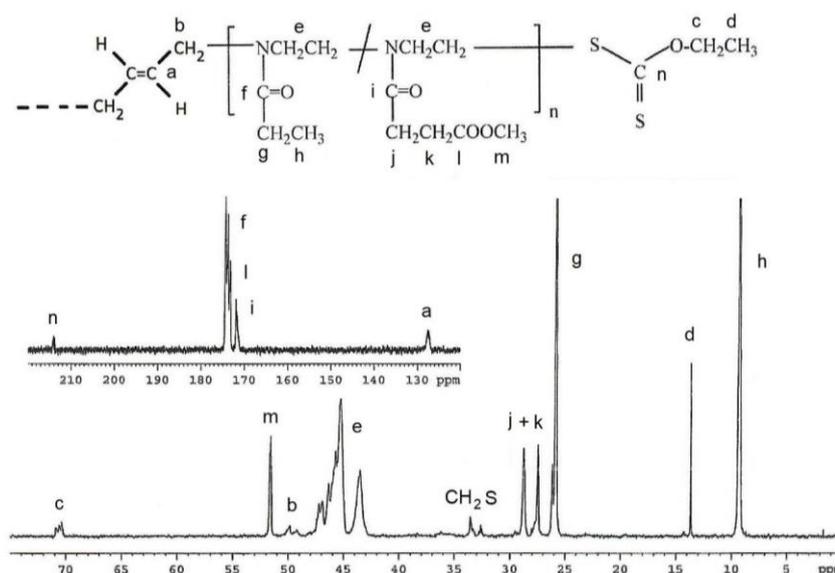
**Table 1.** Synthesis of telechelic polymers. Reaction conditions and results.

Polymer <sup>a</sup>	Mi/DBB <sup>b</sup>	Mf/DBB <sup>c</sup>	Mn(RMN) <sup>d</sup>	Esteroxa <sup>e</sup>	F <sup>g</sup>
PA1	22	25	3040	18	64
PA2	25	29	3380	19	69
PA3	22	25	2770	_f	80
PA4	24	24	3160	35	82
PB1	21	22	.....	22	69
PB2	22	23	.....	56	98

a) Name of the telechelic polymer with ethyl xanthate groups (PA) and vinyl groups (PB), b) Initial molar ratio (Etoxa + Esteroxa)/Initiator, c) Degree of polymerization = Experimental molar ratio (Etoxa + Esteroxa)/Initiator in the telechelic polymer obtained via quantitative <sup>1</sup>H NMR analysis, d) Molecular weight obtained from the degree of experimental polymerization of the telechelic obtained via the <sup>1</sup>H NMR spectrum, e) Molar percentage of Esteroxa in the telechelic polymer (<sup>1</sup>H NMR), f) In the case of PA3, only Etoxa was used, g) Functionalization of the telechelic polymer obtained by <sup>1</sup>H NMR through the comparison between the “c” signal of the ethyl xanthate groups (or the “k and l” signals of the vinyl groups) and the “a” and “b” signals of the initiator.



**Figure 2.** <sup>1</sup>H NMR spectrum of the telechelic polymer PA2 (Etoxa (81 mol%) and Esteroxa (19 mol%), 2n = 29) terminated with ethyl xanthate groups. Functionalization with ethyl xanthate = 69%.



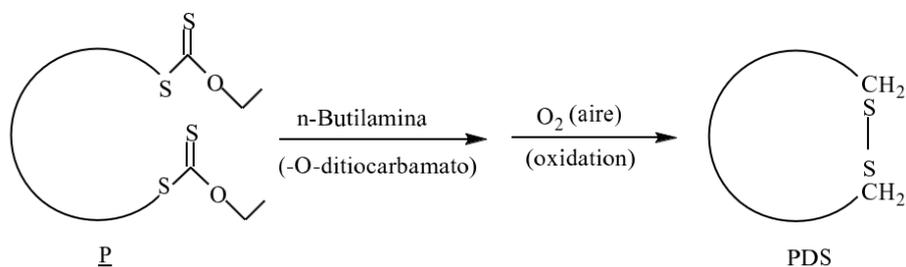
**Figure 3.** <sup>13</sup>C NMR spectrum of the telechelic polymer PA1 (2n = 25) end-functionalized with ethyl xanthate groups. Xanthate functionalization = 64%.

In all experiments, acetonitrile was always used as a solvent, and the reaction temperature and time were 78 °C and 5.5 h, respectively.

The molecular weight and molecular weight dispersion values were 2600 and 1.35 and 2500 and 1.32 for PA1 and PA2, respectively. These values were obtained by gel permeation chromatography (GPC). An initial molar ratio of 20% Esteroxa and 80% Etoxa was used for all copolymers, except for PA4, where 40% Esteroxa and 60% Etoxa were used. For PB1, 20% Esteroxa and 80% Etoxa were used, and for PB2, 50% Etoxa and 50% Esteroxa were used, respectively.

Additionally, a modification reaction of the telechelic polymers PA1 and PA2 was carried out. The cyclization reaction of the telechelic polymer was performed by aminolysis of the ethyl xanthate group with an excess of n-butylamine, obtaining thiol

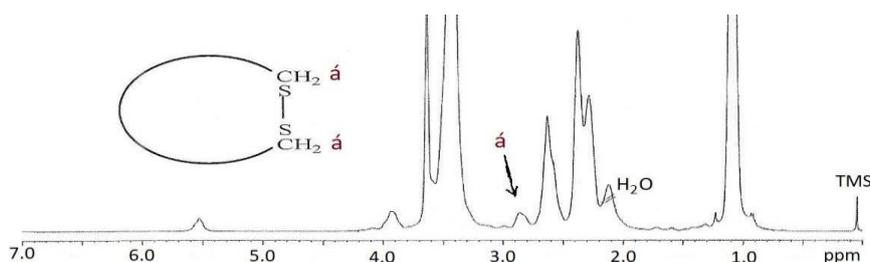
groups at the chain ends, and then these groups were oxidized with atmospheric oxygen in tetrahydrofuran to finally obtain disulfide groups that closed the polymer structure, thus obtaining cyclic polymers (**Scheme 2**).



**Scheme 2.** Cyclization reaction of polymers PA1 and PA2. Where  $P = \text{PA1}$  or  $\text{PA2}$ .

It should be mentioned that the aforementioned reaction was carried out under highly dilute conditions, according to literature data [14], to statistically avoid dimerization of the polymers (intermolecular reaction) and maximize cyclization via the polymer's intramolecular reaction.

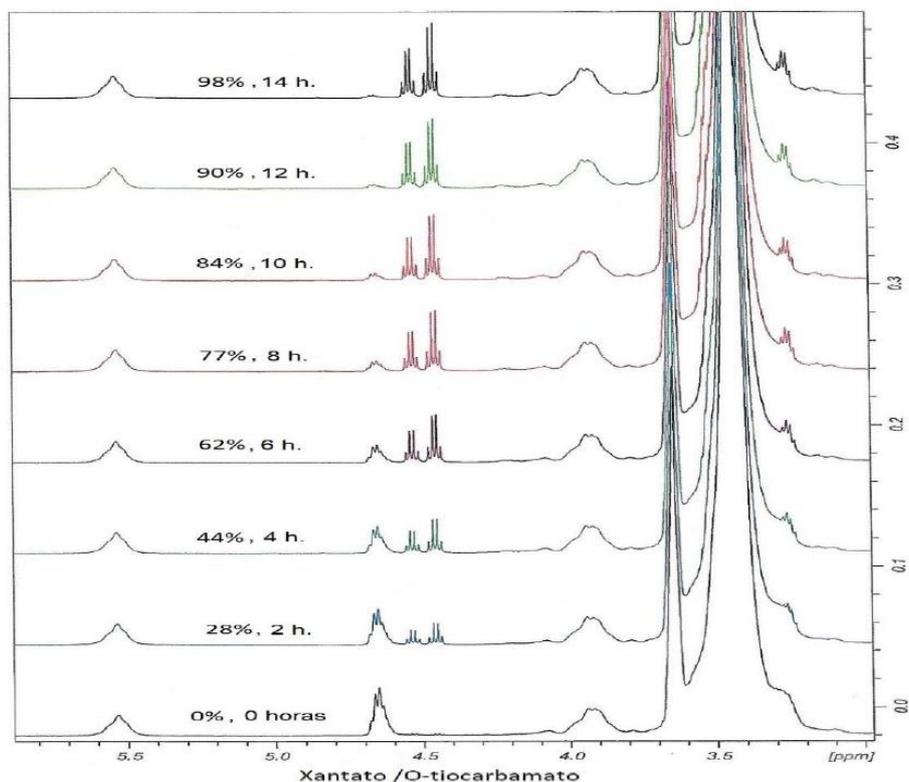
In the  $^1\text{H}$  NMR spectrum of the cyclized polymers, the disappearance of the signals corresponding to the methyl and methylene groups of the ethyl xanthate potassium salt at 1.4 and 4.5 ppm, respectively, was observed, along with the appearance of the signal from the disulfide methylene groups ( $-\text{CH}_2\text{-S-S-CH}_2-$ ) at 2.8 ppm (**Figure 4**). The cyclization reaction of PA2 was studied by the NMR technique, and a sequence of  $^1\text{H}$  NMR spectra was obtained in which it was observed, as time passed, the gradual disappearance of the signals of the ethyl xanthate groups and the simultaneous appearance of the signals of the O-thiocarbamate group (cyclization product) and the disulfide group at 2.8 ppm (**Figures 5 and 6**).



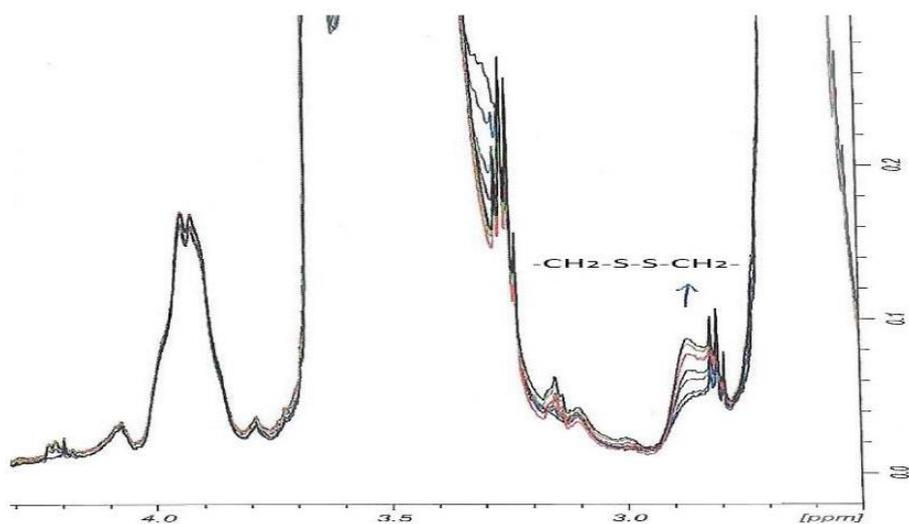
**Figure 4.**  $^1\text{H}$  NMR spectra of telechelic polymer PA1 after cyclization. The disappearance of signals corresponding to the ethyl xanthate group at 1.4 and 4.65 ppm is observed.

It should be mentioned that in the  $^1\text{H}$  NMR spectrum of telechelic polymers, this signal is also observed, albeit more weakly (signal at 2.8 ppm, **Figure 2**). Therefore, it is possible that during the synthesis of the telechelic polymer, a higher functionalization with xanthate groups was initially achieved. Still, this functionalization decreased during the polymer purification process, likely due to partial hydrolysis of the ethyl xanthate group. It is known from the literature that compounds containing sulfur atoms, such as xanthates, disulfides, thiols, etc., are chemically volatile [15,16].

The interest in obtaining cyclic polymers lies in their potential applications, such as adsorption onto metallic nanoparticle surfaces—for example, iron nanoparticles—enabling high stability of such systems [14].



**Figure 5.** Sequence of  $^1\text{H}$  NMR spectra of PA2 during the cyclization process. A yield of 98% was obtained after 14 h of reaction conducted in the NMR tube.

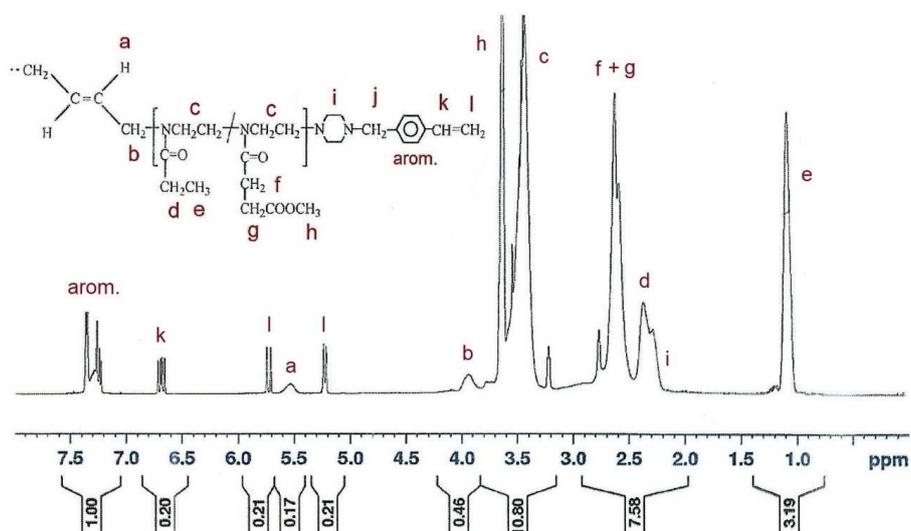


**Figure 6.** Sequence of  $^1\text{H}$  NMR spectra of PA2: An increase in disulfide groups within the telechelic polymer is observed for the cyclization reaction.

### 3.2. Synthesis and characterization of telechelic copolymers with vinyl terminal groups

Telechelic polymers of Etoxa and Esteroxa containing vinyl end groups were also synthesized. This was achieved through cationic ring-opening polymerization of the aforementioned monomers, initiated by dibromobutene (DBB) in acetonitrile, with termination carried out using 4-vinylbenzylpiperazine (4-VBP) (Scheme 1, case 2). This method successfully introduced vinyl groups at the chain ends. The resulting telechelic polymers were designated PB1 and PB2. The results are summarized in **Table 1**.

NMR spectra analysis of these polymers determined that PB1 and PB2 had polymerization degrees of 22 and 23, respectively, with Esteroxa contents of 22% and 56% molar—consistent with theoretical values of 25% and 50% molar—and functionalization degrees of 69% and 98%, respectively (**Figure 7**). The 98% functionalization was achieved when a 600% excess of terminating agent (4-VBP) was used in the termination step, as this statistically drove the reaction between the terminating agent and the propagating chain. In contrast, equimolar termination yielded only 69% functionalization.



**Figure 7.** <sup>1</sup>H NMR spectrum of telechelic polymer PB2 (44 mol% Etoxa, 56 mol% Esteroxa,  $2n = 24$ ) terminated with vinyl groups. Approximate vinyl functionalization = 98%.

### 4. Conclusion

New telechelic polymers were synthesized via ring-opening polymerization of 2-ethyl-2-oxazoline and 2-ester-2-oxazoline, terminated with potassium ethyl xanthate and 4-vinylbenzyl piperazine. These telechelic polymers contained ethyl xanthate or vinyl groups at their chain ends. The maximum functionalization achieved with ethyl xanthate groups was 82 mol%, possibly due to the instability of the ethyl xanthate terminal groups at the chain end. The telechelics with xanthate groups were cyclized through an aminolysis reaction with n-butylamine, followed by oxidation of the generated thiols with oxygen. Cyclic copolymers containing disulfide groups were formed. On the other hand, with the polyoxazoline telechelic polymers containing

vinyl groups at their chain ends, 98% functionalization with these groups was achieved when a large excess of the terminating agent was used.

**Author contributions:** Conceptualization, JCR and HGH; methodology, JCR; software, JCR and HGH; validation, HCR and HGH; formal analysis, HGH; investigation, HGH; resources, HGH; data curation, JCR and HGH; writing—original draft preparation, JCR and HGH; writing—review and editing, JCR and HGH; visualization, JCR; supervision, HGH; project administration, HGH; funding acquisition, JCR. All authors have read and agreed to the published version of the manuscript.

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**Conflict of interest:** The authors declare no conflict of interest.

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