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SYNTHESIS AND CHARACTERIZATION OF POLY(1-METHYLTRIMETHYLENE CARBONATE) (PMTMC) BY MEAN RING-OPENING POLYMERIZATION

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ABSTRACT

In this work, the activity of samarium (III) acetate ($Sm(OAc)_3$) was evaluated as a possible initiator in the ring opening polymerization (ROP) of 1-methyltrimethylene carbonate (MTMC). The effects of temperature (Tr) and monomer-initiator molar ratio (M/I) on the molecular characteristics (conversion, dispersity, and molar mass) of the polymers obtained were analyzed. The reaction temperature was varied between 90 and 160 °C and the molar ratio M/I between 200 and 1000. The molar mass of the products was obtained by size exclusion chromatography (SEC), while its structure was analyzed using FT-IR and ^{1}H-NMR spectroscopy. Thermal polymerization experiments (in the absence of an initiator) were performed in order to evaluate the effectiveness of the initiator. The comparison between the thermal polymerization of MTMC and its polymerization in the presence of $Sm(OAc)_3$, suggests that acetate has very low catalytic activity as the initiator of the ROP of PMTMC. The molar masses of the polymers obtained ranged between 6000 and 10000 Dalton, and the monomer to polymer conversions varied between 9 and 30 %. SEC chromatograms showed monomodal and symmetric curves, suggesting that only one type of active species participates in the polymerization process. Based on the structural analysis, a polymerization mechanism was proposed in which the water possibly acts as the only active species that initiates the reaction.

Keywords: samarium (III) acetate, ring-opening polymerization, 1-methyltrimethylenecarbonate, poly(1-methyltrimethylenecarbonate).

SÍNTESIS Y CARACTERIZACIÓN DE POLI(1-METILTRIMETILENCARBONATO) (PMTMC) MEDIANTE POLIMERIZACIÓN POR APERTURA DE ANILLO

RESUMEN

En este trabajo se evaluó la actividad del acetato de samario (III) ($Sm(OAc)_3$) como posible iniciador en la polimerización de apertura de anillo (PAA) del carbonato de 1-metiltrimetileno (MTMC). Se analizaron los efectos de la temperatura

(Tr) y relación molar monómero-iniciador (M/I) sobre las características moleculares (conversión, dispersidad y masa molar) de los polímeros obtenidos. La temperatura de reacción se varió entre 90 y 160 °C y la relación molar M/I entre 200 y 1000. La masa molar de los productos se obtuvo mediante cromatografía de exclusión por tamaño, mientras que su estructura fue analizada mediante espectroscopia FT-IR y ^{1}H-RMN. Además, se realizaron algunos experimentos de polimerización térmica (en ausencia de iniciador) que sirvieron de referencia para evaluar la efectividad del iniciador. La comparación de los resultados obtenidos en la polimerización térmica y en presencia del $Sm(OAc)_3$ indicó que este último presenta muy poca actividad catalítica como iniciador de la PAA de PMTMC. Las masas molares de los polímeros obtenidos oscilaron entre 6000 y 10000 Dalton, mientras que las conversiones de monómero a polímero variaron entre 9 y 30%. Los cromatogramas SEC mostraron curvas mono-modales y simétricas, indicando que en el proceso de polimerización participa un solo tipo de especie activa. En base al análisis estructural, mediante técnicas espectroscópicas, se propuso un mecanismo de reacción para la polimerización en la que el agua posiblemente actúa como la única especie activa iniciadora de la reacción.

Palabras clave: acetato de samario (III), polimerización por apertura de anillo, 1-metiltrimetilencarbonato, poli(1-metiltrimetilencarbonato).

SÍNTESE E CARACTERIZAÇÃO DO POLI(CARBONATO DE 1-METILTRIMETILENO) (PMTMC) POR POLIMERIZAÇÃO POR ABERTURA DE ANEL

RESUMO

Neste trabalho avaliou-se a activida do acetato de samário (III) ($Sm(OAc)_3$) como possível iniciador na polimerização de abertura de anel (PAA) de 1-metiltrimetilencarbonato (MTMC) nós foram avaliados. Os efeitos da temperatura de reacção (Tr) e a proporção molar de monómero para iniciador (M/I) nas características moleculares dos polímeros obtidos foram analisados: MTMC conversão de poli (1-metiltrimetilencarbonato) (PMTMC), dispersidade e massa molar. A temperatura da reacção variou entre 90 e 160 °C e e a relação molar M/I entre 200 e 1000. A massa molar dos produtos da reacção obteve-se por cromatografia de exclusão de tamanho, ao passo que a sua estrutura foi analizada por espectroscopia de FT-IR e RMN de ^{1}H. Além disso, alguns experimentos de polimerização térmica foram realizados (na ausência de um iniciador), a fim de servir como referência para avaliar a eficácia do iniciador. A comparação dos resultados obtidos na polimerização térmica e na presença de $Sm(OAc)_3$ indicou que este último apresenta muito pouca atividade catalítica como iniciador do PAA do PMTMC. As massas molares dos polímeros obtidos variaram entre 6000 e 10000 Dalton, enquanto as conversões de monômero para polímero variaram entre 9 e 30 %. Os cromatogramas de SEC mostraram curvas monomodais e simétricas, indicando que no processo de polimerização, apenas um tipo de espécie ativa participa. Com base na análise estrutural, utilizando técnicas espectroscópicas, foi proposto um mecanismo de reação para polimerização, no qual a água possivelmente atua como a única espécie ativa que inicia a reação.

Palavras chave: acetato de samário (III), polimerização de abertura de anel, 1-metil-trimetilenocarbonato, poli (1-metil-trimetilenocarbonato).

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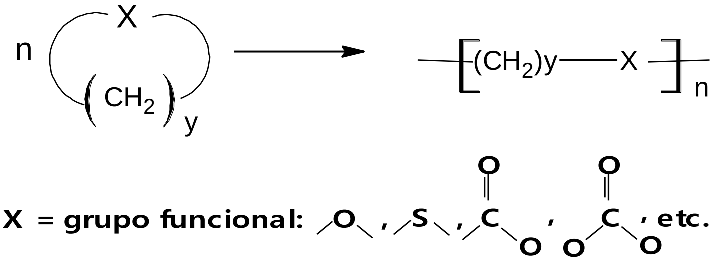
1. INTRODUCTION

Generally, the cyclic molecules or rings have tension in their bonds, because of their geometry, the lengths and angles of bonds do not match those of stable non-cyclic molecules. Therefore, a cycle in tension is equivalent to a bifunctional molecule due to its ability to open the ring by breaking one of its bonds, joining each resulting end with other molecules and thus forming a pair of new bonds that allow the tension of the ring to relax (Horta, 1991; Odian, 2004). In this way, the ring-opening polymerization (ROP) can be defined as the process in which a cyclic monomer is transformed to linear polymer chains by means of its opening and in the presence of a catalyst (**Scheme 1**) (Odian, 2004):



Scheme 1. General reaction of ring-opening polymerization (ROP).

The main monomers polymerizable by ROP are heterocyclic compounds (epoxides, sulfides, lactones, cyclic carbonates, etc.) (Horta, 1991; Odian, 2004; Okada, 2002), which give rise to materials with excellent mechanical properties and that also result to be biocompatible and biodegradable materials, with a wide variety of applications, including sutures, drug liberators, resorbable prostheses, and even agricultural membranes, among many others (Nair & Laurencin, 2008; Penczek et al., 2007; Vroman & Tighzert, 2009).

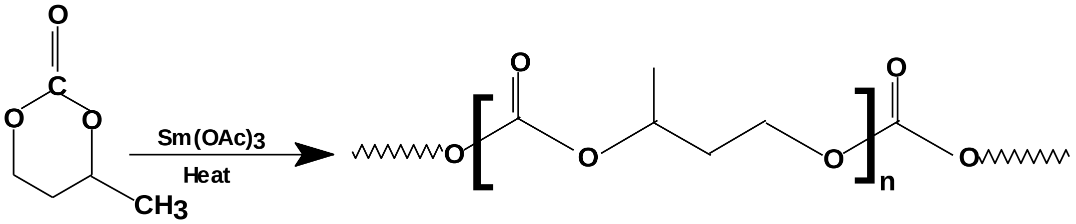
In this way, various types of polymers (aliphatic polyesters, polycarbonates, polyethers, polyamides and polyurethanes) are obtained by ROP, with good control of the properties (molar mass and dispersion) that are desired in the material and its structure (homopolymer, diblock copolymers, multiblock, random, among others) (Jerome & Lecomte, 2008; Nair & Laurencin, 2008; Vroman & Tighzert, 2009; Yamashita, 1978). The growing interest in this type of polymerization has led to numerous investigations, whose main objective is the development of new polymerization initiators that produce biodegradable polymers with well-controlled molecular architecture and defined molar mass (Albertson & Varma, 2003).

In the case of heterocyclic monomers, the presence of heteroatoms provides a site in which a nucleophilic or electrophilic attack by an initiating species can occur, and thus a large variety of cationic, anionic and coordination initiators have been reported as useful for developing the ROP

(Albertson & Varma, 2003; Jerome & Lecomte, 2008; Penczek et al., 2007). Generally, ionic initiators are the most reactive, and in the case of the polymerization of lactones and cyclic carbonates are responsible for producing inter and intramolecular transesterification reactions, which results in a decrease in the molecular weight of the polymer, and therefore originate wide molecular weight distributions (Keul et al., 1986; Kühling et al., 1989, 1990, 1992; Matsuo et al., 1998; Murayama et al., 1998; Pawłowski & Rokicki, 2004; Wurm et al., 1992). Due to this, at present, the coordination compounds with metals such as Al, Sn, Nd, Y, Yb, Sm, La, Fe, Zn, Zr, Ca, Ti and Mg are being used in the synthesis and control of polymerization reactions instead of ionic initiators (Albertson & Varma, 2003; Jerome & Lecomte, 2008). It has been shown that the coordination compounds impart greater control in the polymerization reactions by the moderate nucleophilicity and relatively high acidity that characterizes them. However, many of the metals from which this type of initiators are derived have toxicity and, given their difficulty in completely removing them from the polymer obtained, they remain as impurities inside the material, which could give rise to unpredictable problems in the systems where they are used. For this reason, it has been placed emphasis on the development of initiators with structures and metal centers that are relatively low toxicity, that are ecologically benign and that their residues are potentially harmless (Gowda & Chakraborty, 2009).

Currently, the catalysts obtained from rare earths are probably those that have attracted the most attention due to their high activity, low toxicity and even their easy removal of the synthesized products (Ling & Shen, 2002; Ling et al., 2010; C. Yu et al., 2004). In general, the use of rare earth metal complexes as initiators have shown superiority, since there is a wide variety of reports in which high molecular weights are obtained with narrow distribution curves compared to other catalysts (Tsutsumi & Yasuda, 2001).

In our laboratory, compounds $Sm(OAc)_3$ and samarium (III)–amino acid had been used as initiators for ROP of lactones and carbonates cyclic, obtaining satisfactory results (Contreras-Ramírez & Monsalve, 2019; Contreras-Ramírez et al., 2019; Contreras et al., 2013; Medina et al., 2018; Monsalve et al., 2015). In this work, the catalytic activity of samarium (III) acetate ($Sm(OAc)_3$) was explored as a possible initiator of ROP of MTMC. In order to establish those reaction parameters that would lead to the highest conversions of monomer to polymer with the highest molar mass and with narrow molar mass distributions, a systematic study of the mass homopolymerization of the MTMC was carried out, varying the reaction conditions: temperature (Tr), molar monomer-initiator ratio (M/I).



Scheme 2. ROP of MTMC using samarium (III) acetate as a possible initiator.

2. METHODOLOGY

2.1. Materials, solvents and reagents

1,3-Butanediol (Sigma-Aldrich, 99%) was purified by fractional distillation under reduced pressure (160°C to 5 mmHg). Methanol (99.3%), chloroform (99.8%) (both, J.T. Baker) were used without prior purification. Samarium acetate ($Sm(CH_3CO_2)_3$ x H_2O) (99.9%, Aldrich) was used without previous purification, but it was dried for two hours before its use. Nitrogen (AGA, UAP grade) was used without any previous purification. The monomer (MTMC) was synthesized and purified according to the method described by Monsalve & Contreras, 2014. A mixture of 1.0 mole of 1,3-butanediol, 1.19 mole of diethylcarbonate and 0.1 g of metallic sodium was refluxed at 130 °C for 6 h. The ethanol formed was then removed by distillation; and then with the purpose of removing residual diethylcarbonate, it was applied vacuum to the system (35 mmHg) maintaining the temperature around 130 °C. Finally the remaining crude reaction product was distilled under vacuum at high temperatures (> 170 °C, 5 mmHg) in the presence of a few drops of tin octanoate ($Sn(Oct)_2$) and a small amount of calcium hydride (CaH_2) (Florjańczyk et al., 2006; Wang et al., 1998). The MTMC was obtained as a viscous liquid and was collected on molecular sieve (Tsutsumi & Yasuda, 2001). For storage, it was kept in a vacuum desiccator.

2.2. Synthesis and purification of PMTMC

Pre-established amounts of the monomer and the catalyst were introduced into a pyrex glass reactor equipped with a magnetic stirrer. The reactor was purged with nitrogen to finally seal it and introduce it in an oil bath at the previously fixed reaction conditions (Tr and reaction time). In all cases, the polymers obtained were purified by the dissolution/precipitation method using chloroform as solvent and methanol as non-solvent. Finally, the polymer samples were dried at 40 °C, under reduced pressure, for 24 h. The conversion of TMC to PTMC was obtained by gravimetric measurements of the precipitated polyester.

2.3. Characterization of the obtained polymers

2.3.1. Infrared Spectroscopy with Fourrier Transform (FTIR)

The FTIR spectra were recorded in a Perkin-Elmer model 2000 spectrophotometer, from films obtained by evaporation of their chloroform solutions, on NaCl windows. The spectral range used was between 400 and 4000 cm^{-1}.

2.3.2. Nuclear magnetic resonance (NMR) spectroscopy

The spectra for the samples synthesized in this work were recorded in a Bruker NMR spectrometer, model Avance DRX 400MHz. The samples were dissolved in deuterated chloroform (CDCl3, δ= 7.26 ppm) and tetramethylsilane (TMS) was used as an internal reference.

2.3.3. Size Exclusion Chromatography (SEC)

A Waters GPC chromatograph, model 150 CV, equipped with refractive index and viscosimetry detectors, was used, coupled to a Compaq computer with which the calculations were carried out using a program called Milenium 32. Analyzes were performed using columns filled with Ultrastyragel of permeability 10^3, 10^4 and 10^5 Å at 40 ºC with tetrahydrofuran (THF) as solvent. The equipment was calibrated with monodisperse polystyrene patterns of different molecular weight. For each analysis, 8 mg of the sample was weighed and dissolved in THF.

3. RESULTS AND DISCUSSION

In the first place, the qualitative analysis of the physical aspect of the products obtained in the polymerization reactions was carried out, in order to compare them with those of the monomer and thus record the changes that occurred as a result of the polymerization process occurred. Unlike the MTMC (viscous liquid, boiling temperature: 100-105 °C to 1 mmHg), the reaction products obtained were very sticky, translucent and practically colorless solids. This result would indicate that the formation of PMTMC occurred.

3.1. Effect of the reaction temperature (T_r)

Given that the MTMC is a liquid that has a very high boiling point, the temperature was chosen as the first reaction parameter to be analyzed. A reaction time of 24 hours and the M/I ratio= 600 were used; these parameters were selected according to the bibliography consulted (Ling & Shen, 2002; Ling et al., 2010; Tsutsumi & Yasuda, 2001).

Some thermal polymerization experiments (in the absence of the initiator) were carried out to take as a reference and evaluate of the effectiveness of the initiator in this polymerization. In **Table 1**, the different experiences carried out are shown. As can be seen at temperatures below 120 °C (Exp. JM-1, JM-5 and JM-6), $Sm(OAc)_3$ shows no activity as an initiator towards the polymerization of the

MTMC. This behavior may be associated with the fact that polymerization takes place in the absence of solvent; therefore decreasing the reaction temperature increases the viscosity of the reaction medium, which causes a decrease in the mobility of the growing species and therefore the activity of polymerization propagating species decrease.

Table 1. Effect of T_r on the ROP of MTMC

Exp.	**T_r (°C)**	**$\overline{M_n}$x10^{-3} (g/mol)$^{(a)}$**	**$Đ_M$ $^{(b)}$**	**Conversion (%)$^{(c)}$**
JM-1$^{(d)}$	90	-	-	0
JM-2$^{(d)}$	120	9.81	1.28	17.4
JM-3$^{(d)}$	140	9.59	1.24	19.1
JM-4$^{(d)}$	160	8.92	1.23	9.30
JM-5	90	-	-	0
JM-6	100	-	-	0
JM-7	120	9.92	1.18	23.9
JM-8	140	10.73	1.23	23.4
JM-9	160	6.92	1.30	14.5

(a) Molar mass average in number; **(b)** Dispersity; **(a)** and **(b)** determined by SEC; **(c)** Based on the amount of initial monomer, % Conv= (g_{PMTMC}/g_{MTMC}) x 100; **(d)** thermal polymerization, in the absence of initiator. MTMC = 1 mL ($9.23x10^{-3}$ mol, 1.0615 g), t_r = 24h, M/I= 600 (0.0059 g of Sm(OAC)$_3$).

At Tr≥120 °C the conversions of monomer to polymer are slightly higher when the reaction is performed in the presence of the initiator (Exp. JM-7, JM-8 and JM-9) than in the thermal polymerization (Exp. JM-2, JM-3 and JM-4), suggesting that Sm(OAc)$_3$ shows some catalytic activity in this polymerization, which is not very high compared to that was observed in the polymerization of ε-caprolactone, L-lactide and trymethylene carbonate (Contreras & Monsalve, 2019; Contreras-Ramírez et al., 2019; Contreras et al., 2013). Also, it can be noted that at 160 °C (Exp. JM-4 and JM-9), the conversion and the molar mass of the PMTMC obtained decrease, which could be indicating that thermal degradation processes occur (Ling & Shen, 2002; Save et al., 2002; Wang et al., 2013).

On the other hand, in the **Figure 1** are shown in a comparative form, the SEC chromatograms of the reaction products obtained without and with initiator, observing that there is no marked difference in the molar masses and dispersity of the PMTMCs obtained in both types of experiments.

All SEC chromatograms show a mono-modal molar mass distribution whose dispersity ($Đ_M$) oscillates between 1.18 and 1.30. This fact would indicate that in the polymerization process, only one active species participates. Furthermore, in Figure 1 it can also be seen that at 160 °C the molar mass of the polymer obtained in the absence of initiator (JM-4) is higher than that obtained with Sm(OAc)$_3$ (JM9), which could be associated with the fact that this initiator at high temperatures could also catalyze the depolymerization reactions for this monomer (Rokicki et al., 2003).

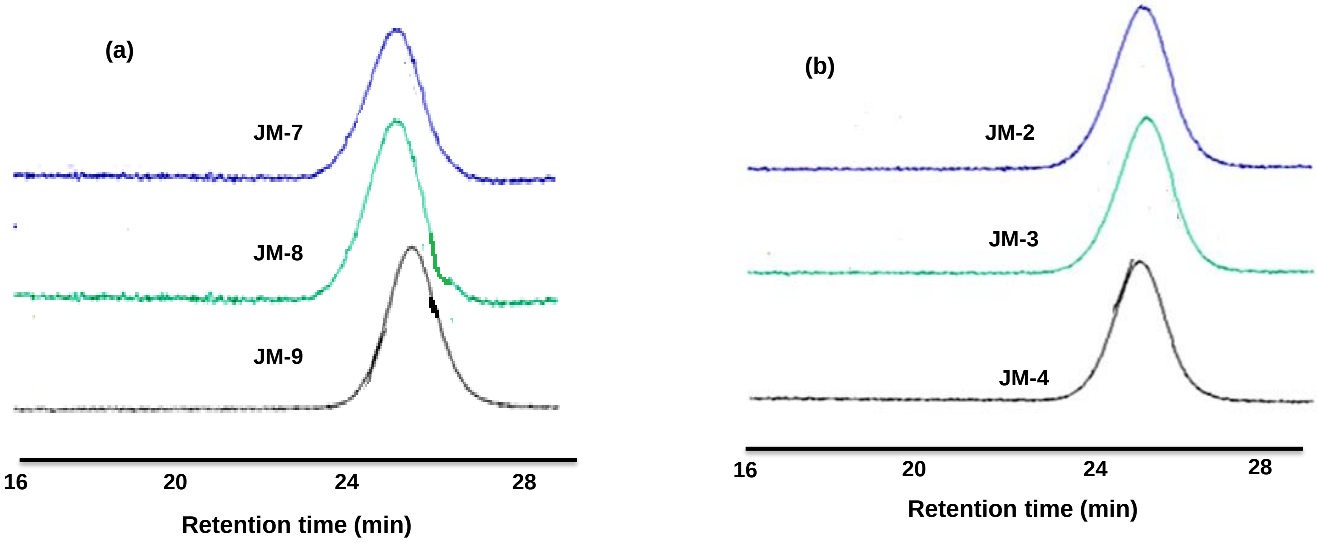


Figure 1. Comparison of the SEC curves for the series of PMTMC obtained by varying the temperature: (a) in the presence of $Sm(AcO)_3$; (b) absence of the catalyst (thermal polymerization)

3.2. Effect of the M/I ratio

The effect of the $MTMC/Sm(OAC)_3$ (M/I) molar ratio between 200 and 1000 was analyzed; taking into account the results shown in **Table 1**, it was chosen 140 °C as Tr and the reaction time used was 24 h. The results obtained are shown in **Table 2**.

Table 2. Results of the polymerizations varying the M/I ratio

Exp.	M/I	$Sm(AcO)_3$ (mg)	$Sm(AcO)_3$ (mmol $x10^{-3}$)	$\overline{M}_n x10^{-3(a)}$ (g/mol)	$Đ_M$ [(b)]	Conversion (%) [(c)]
JM-10 [(d)]	-	-	-	9.59	1.24	24.1
JM-11	1000	3.52	9.23	9.11	1.27	27.3
JM-12	800	4.40	11.53	8.70	1.24	30.3
JM-13	600	5.87	15.38	10.36	1.23	26.4
JM-14	400	8.80	23.07	9.99	1.26	26.1
JM-15	200	17.61	46.16	10.48	1.23	19.3

(a) molar mass average in number; **(b)** dispersity; (a) and **(b)** determined through SEC; **(c)** based on the initial amount of monomer, % Conv= (g_{PMTMC}/g_{MTMC}) x 100; **(d)** thermal polymerization, in the absence of initiator. MTMC = 1 mL ($9.23x10^{-3}$ mol, 1.0615 g), T_r = 140 °C, t_r = 24h.

It can be noted that between M/I= 400 and 1000, the values of conversion of monomer to polymer and of molar mass, vary very little with each other. This fact would be indicating, again, that the $Sm(OAc)_3$ shows little activity as an initiator in the polymerization of the MTMC and that the reaction seems to take place predominantly via thermal polymerization. When a high amount of $Sm(OAc)_3$ (M/I= 200) was used, the conversion decreases to 19%, possibly due to an increase in transesterification reactions (Rokicki et al., 2003), suggesting again that they could be catalyzed by the initiator. This can generate the formation of chains or oligomers that could dissolve in methanol during the polymer precipitation process, decreasing the conversion of monomer to polymer.

The similarity in molar mass and dispersity values of the different products obtained can be observed more clearly in **Figure 2**, in which the evolution of size exclusion chromatograms (SEC) as a function of the molar ratio M/I is shown

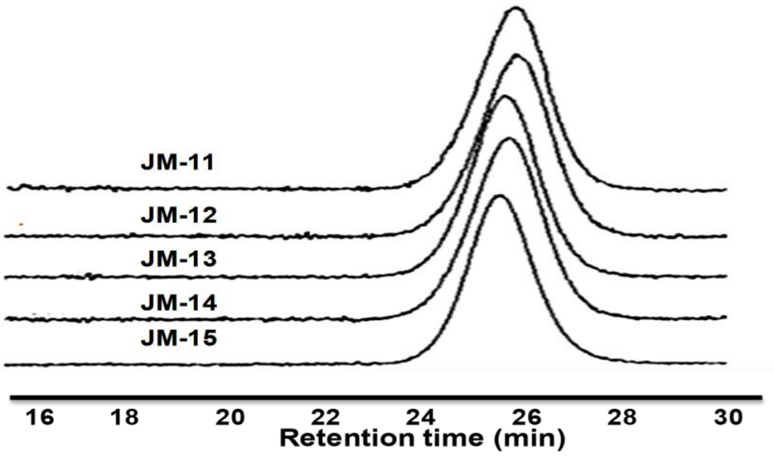
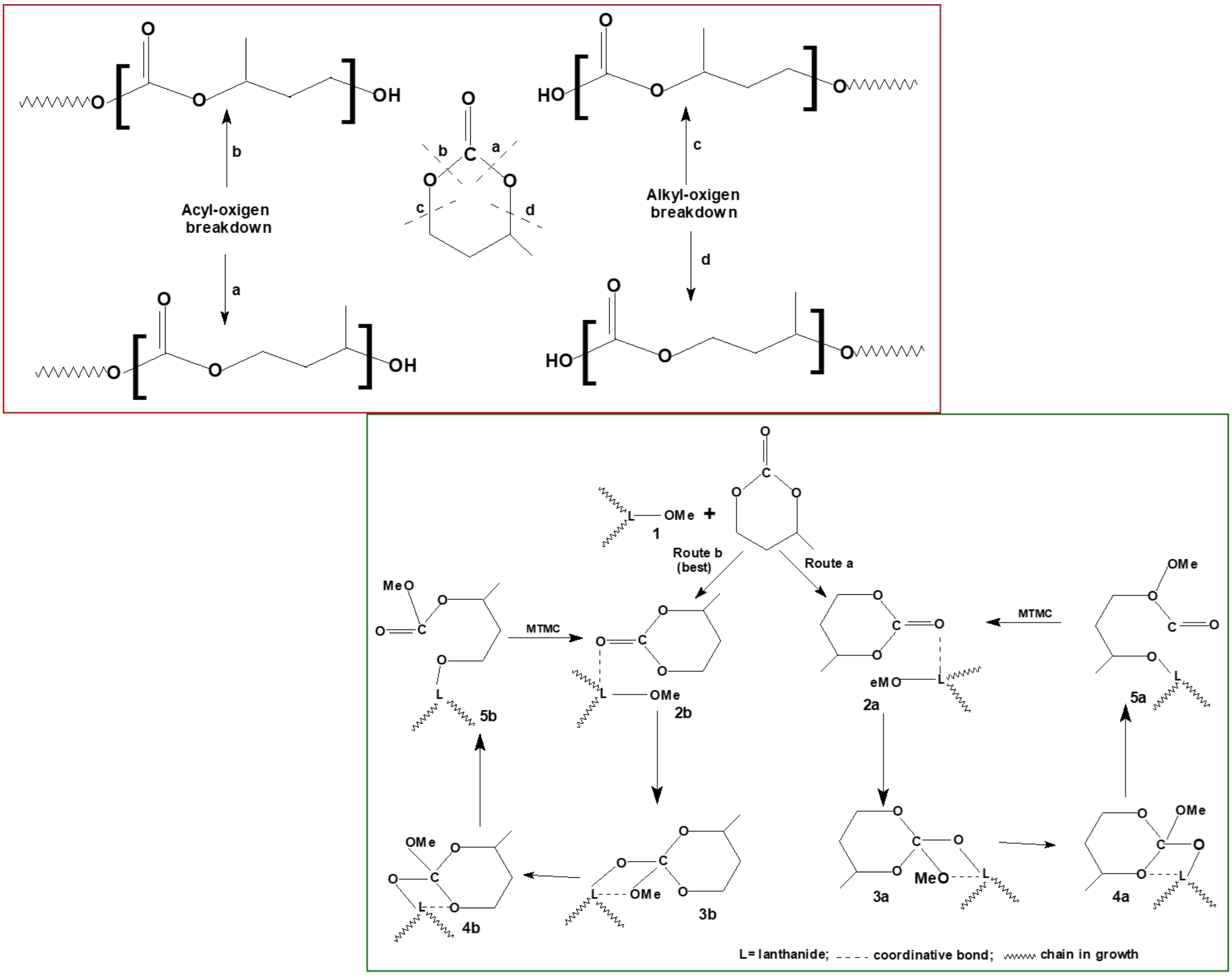


Figure 2. Evolution of the SEC curves with the M/I ratio

All SEC curves are mono-modal and symmetric, with a moderate dispersity (**$Đ_M$**) around 1.25 and a molar mass around 10000 g/mol. This behavior, again indicates, the participation of a single active species in the polymerization process.

In general, the results obtained indicate that $Sm(OAc)_3$ shows little activity as an initiator in the polymerization of the MTMC. Similar results were obtained by other authors (Ling et al., 2010), when they carried out the study of the polymerization of this monomer in the presence of different initiators type organolanthanides. They proposed that this behavior was related to the asymmetry of the MTMC ring, which resulted in its polymerization mechanism passing through the different routes; as shown in **Scheme 3** (Ling et al., 2010).

On the other hand, taking into account the proposed coordination-insertion mechanism for this type of polymerization (Contreras et al., 2013; Contreras et al., 2019), it is very likely that in this case the steric effect generated by the proximity of the methyl group to the group carbonate is affecting. Another fact that justifies the results presented above and that must be taken into account is the insolubility of the initiator in the monomer. This factor directly influences the polymerization process because adequate dispersion of one in the other will not occur (Tsutsumi & Yasuda, 2001). This insolubility prevents the monomer and the initiator from coming into contact with each other, so that the activation of the monomer does not occur or only partially does so, therefore, the polymerization process develops to a lesser extent.



Scheme 3. Mechanisms of polymerization of the MTMC

3.3. Structural analysis

The structural characterization of the reaction products obtained was carried out by infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance (^{1}H-NMR).

3.3.1. FT-IR spectroscopy

In **Figure 3** comparatively shows the FT-IR spectra of the MTMC and that of one of the polymers obtained, and the assignments of the highlighted bands is presented in **Table 3** (Hesse, Meier & Zeeh, 1995).

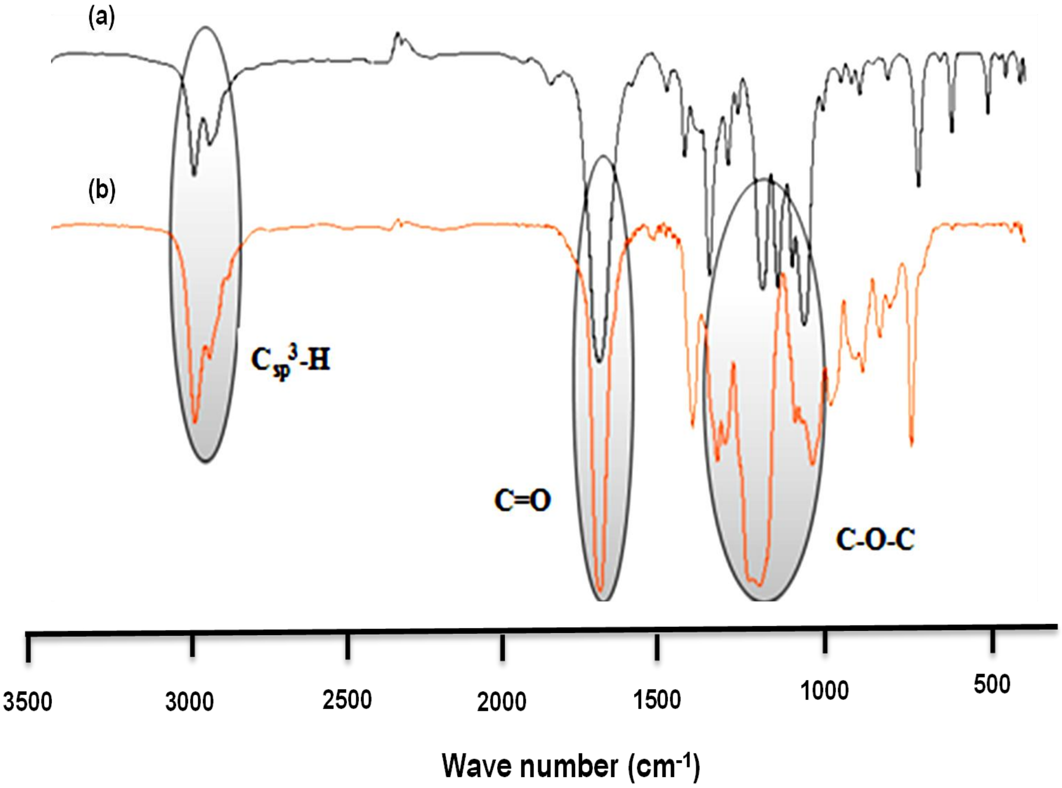


Figure 3. Espectro FT-IR de a) MTMC y b) PMTMC

Table 3. Assignment of the most important bands, observed in the FT-IR spectra of the PMTMC and MTMC

Type of vibration	$\bar{\nu}_{PMTMC}$ **(cm^{-1})**	$\bar{\nu}_{MTMC}$ **(cm^{-1})**
υ (C=O)	1744	1745
υ_s (C-O-C)	1093	1246
υ_{as} (C-O-C)	1255	1176
υ (C_{sp}^3-H)	2981	2984

$\bar{\nu}$: Wave number; υ: stretching; υ_s: symmetrical stretch; υ_{as}: asymmetrical stretch.

The most significant changes in the FT-IR spectra are those observed for the signals caused by the stretching vibrations of the C-O-C bond (between 1000 and 1400 cm^{-1}). It can be seen that the signal corresponding to the symmetric stretch appears at the lower wave number in the polymer ($\bar{\nu}_{PMTMC}$ = 1093 cm^{-1}) that in monomer ($\bar{\nu}_{MTMC}$ = 1246 cm-1); and the other caused by the asymmetric stretch appears wider in the polymer while moving to a higher wave number: ($\bar{\nu}_{MTMC}$ = 1176 cm^{-1} → $\bar{\nu}_{PMTMC}$ = 1255 cm^{-1})

3.3.2. *^{1}H-NMR spectroscopy*

The typical spectrum of the obtained PMTMC is shown together with that of the MTMC, in **Figure 4**. The assignment of each of the signals was made by comparison with values already reported according to the type of bond (Cai et al., 1998; Hesse et al., 1995; Ling et al., 2010; Tsutsumi & Yasuda, 2001).

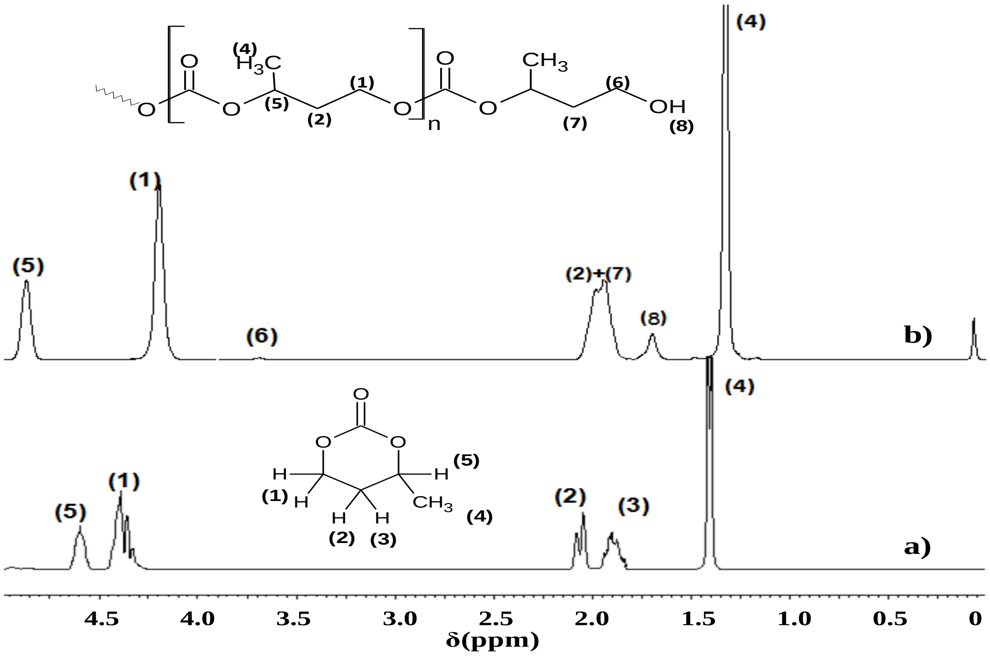


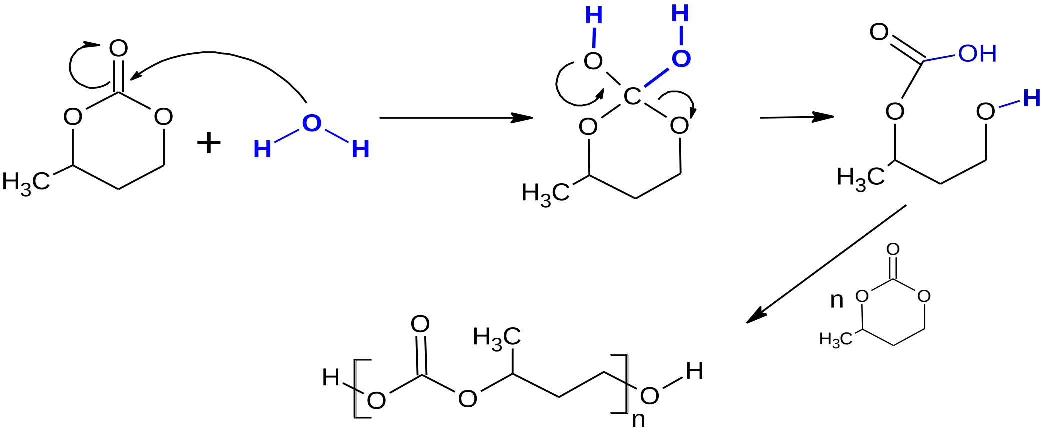
Figure 4. ^{1}H-NMR spectrum of a) MTMC and b) PMTMC

Table 4. Characteristic signals in the ^{1}H-NMR spectrum for the PMTMC

Signal (n°)	Assignment	PMTMC (δ)(ppm)	Multiplicity
1	$-OC\underline{\mathbf{H}_2}CH_2-$	4,20	m
2	$-CH_2C\underline{\mathbf{H}_2}CH_2-$	1,95	m
5	$-CH_2C\underline{\mathbf{H}}CH_3$	4,88	m
4	$-OCHC\underline{\mathbf{H}_3}$	1,33	d
6	$-CH_2C\underline{\mathbf{H}_2}OH$	3,69	m
7	$-C\underline{\mathbf{H}_2}CH_2OH$	≈1,95	m
8	$CH_2CH_2O\underline{\mathbf{H}}$	1,69	s

m: multiplete; s: singlete;

Finally, from the ^{1}H-NMR spectrums, it is possible to carry out the analysis of the end groups of the chain in the PMTMC obtained, and with this information to postulate a possible reaction mechanism for the polymerization (Ling et al., 2010). For this purpose, **Figure 4-b** shows the typical NMR spectrum of the polymers obtained, in which it is possible to observe the characteristic signals of the PMTMC (signals 1, 2, 4 and 5) and two signals of low intensity: one at 3.69 ppm assigned to the hydrogen atoms of the methylene group directly bonded to the oxygen of the terminal hydroxyl group and another relatively broad signal at 1.69 ppm attributed to the hydrogen of the terminal hydroxyl group (signals 6 and 8, respectively). These new signals can be associated with a terminal hydroxy chain end (-C**H**$_2$-C**H**$_2$-O**H**) (Ling & Shen, 2002; Ling et al., 2010). Based on this information and taking into account the low activity of Sm(OAc)$_3$ as initiator, the following reaction mechanism is proposed (**Scheme 4**)



Scheme 4. Mechanism of thermal polymerization for the PMTMC

In this polymerization process, water, either from the humidity of the environment or from residues that have been occluded in the monomer, could act as an initiator of the polymerization reaction. In this mechanism, the carbonyl carbon of the MTMC is attacked by the oxygen in the water followed by the opening of the ring via the breakdown of the acyl-oxygen bond. The propagation of the chain continues through the attack of the oxygen atom of the terminal -OH group on the carbonyl carbon of another monomer molecule. A mechanism similar to this one was proposed by Yu & Zhuo (2004).

4. CONCLUSIONS

The results obtained in this work showed that Sm(OAc)$_3$ has low effectiveness as an initiator in the polymerization of the MTMC, and that in this case the formation of PMTMC proceeds, predominantly, via thermal polymerization. Taking into account that the polymerization was carried out in the absence of organic solvent and that the material obtained was free of initiator residues, the obtained PMTMC can be used as a biomaterial. The study of the polymerization mechanism suggests that the polluting water in the reaction medium plays an important role in the initiation stage of the polymerization process.

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