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Application of Glycerol in the Synthesis of Hyperbranched and Highly Branched Polyethers: Characterization, Morphology and Mechanism Proposal

Diego Botelho Campelo Leite[a,b], Edmilson Miranda de Moura[a], Carla Verônica Rodarte de Moura[a]*

[a]*Universidade Federal do Piauí, Campus Ministro Petrônio Portela, 64049-550, Teresina, PI, Brasil*
[b]*Instituto Federal do Maranhão, 65665-000, São João dos Patos, MA, Brasil*

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Hyperbranched biopolymers is an important class of polymer that is used in different areas, mainly in biomedicine. AB_2 monomers are crucial to the development of a "hyperbranched" architecture of polyglycerol, being glycidol the most commonly used, even considering its environmental hazard. Glycerol carbonate is an ecologically accepted monomer synthesized directly from glycerol, and the chosen for the studies herein. In literature, no studies described the use of glycerol and cyclic carbonates to prepare hyperbranched polymers. This work describes the obtainment of hyperbranched polymers using glycerol and TMP salt as core-initiator and glycerol carbonate and propylene carbonate as monomers. The polymers were characterized by FTIR, NMR, MALDI-TOF and TEM. NMR spectroscopy showed linear, dendritic, and terminal units of hyperbranched polymer. The degree of branching PGLYGC and PTMPGC was 0.669 and 0.667, respectively. The molecular weight of PTMCGC, PTMPPC, PGLYPC was found and compared with MALDI. The molar mass was not different from the calculated by Inverse Gated. These polymers have enormous potential as drug delivery and an environmentally correct synthetic route due to the substitution of glycidol by biocompatible monomers.

Keywords: *Hyperbranched, Dendrimers, Polyglycerol, Propylene Carbonate, Ring Opening Polimerization Mechanism.*

1. Introduction

Over the past decade, attention on the use of biopolymers has grown enormously such as hyperbranched polymers or dendrimers due to proven potential as drug delivery due to biocompatibility, degradability and absorbability properties, and in medicinal engineering[1-3].

The synthesis of dendrimers is very laborious because involves multiple steps of protection/deprotection and complex purification[4]. Hyperbranched polymers are, generally prepared by a one-step self-polymerization of AB_m-type monomers. These polymers are macromolecules with a random branching topology with compact dimensions, which are part of a special class of dendritic macromolecules[5]. They have similar structures and properties to the dendrimer, such as intrinsic compact structure, large number of terminal groups, low viscosity compared to similar straight chain polymers, and high solubility[6].

This class of polymers has the attention of the scientific community due to their capacity as "drug delivery", since it improves important therapeutic properties, such as: insolubility of drugs in water, bioavailability, biocompatibility, biodegradability[7]. Their properties showed to be better in comparison to polyethylene glycol, an industrial drug carrier, due to low toxicity, low immunogenicity as well as due to increasing camouflage against mononuclear phagocyte system (MPS)[8-10].

Glycerol is one of the byproducts of the biodiesel production reaction. This industry has grown considerably in recent years and the amount of glycerol produced has increased greatly. The demand for glycerol by the industries did not increase its use. Thus, the excess glycerol generated by the biodiesel industry has been a problem. Therefore, research in order to use this excess of glycerol is necessary and has been described in the literature. One of the uses of glycerol is in obtaining glycerol carbonate, an important monomer used to obtain hyperbranched polyglycerol (HPG).

Behr et al., discussed that the HPG cannot be synthesized directly from glycerol as feedstock, but HPG could be prepared by using glycidol[11]. Salehpour et al. describe that the production of polyglycerols using glycerol, different catalysts and low pressures, lead to the formation a gel. This approach is a polycondensation reaction[12,13]. Medeiros et al. showed the production of oligomers using different kinds of catalysts in different temperatures. They have used an extensive polymerization of glycerol until obtaining the thermoset resins[14]. The literature has shown the use of glycerol carbonate to obtain some polyhydroxyurethanes[15].

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*e-mail: carla@ufpi.edu.br

Rokicki et al. have described the obtainment of hyperbranched polyglycerol using glycerol carbonate (GC) as starting material and 1,1,1-tris(hydroxymethyl)propane (TMP)[16]. To provide greater functionality for glycerol, which is a 3-hydroxylated polyalcohol such as TMP, one of the possibilities is the use as the main initiator and/or monomer in the synthesis of HPG. To the best of our knowledge, no work relates the obtaining of hyperbranched polyglycerol using glycerol and glycerol carbonate as feedstock. In front of the above reports we have described in this work, the obtainment, characterization and mechanism of hyperbranched polyglycerol using glycerol and 1,1,1-tris(hydroxymethyl)propane salt as initiator (core unit), glycerol carbonate as a AB_2-type monomer and propyl carbonate as a AB_1-type monomer.

2. Materials and Methods

All reagents and solvents were of analytical grade (Sigma-Aldrich) and used without further purification.

Fourier Transform Infrared spectra (FTIR) have been obtained using a Perkin Elmer Spectrum 100 spectrometer with the Fourier transform. Nuclear Magnetic Resonance (NMR) analyses have been obtained using Varian Inova spectrometer at 400 MHz using dimethylsulfoxide-d6. The Inverse Gated analyse has been performed disengaging Nuclear Effect Overhousser "1H decoupling" in a spectral range 25000 Hz with an acquisition time of 0.655 s, relaxation time of 10 s in a pulse from 3.433 microseconds (30) to 89000 scans.

The MALDI-MS analysis have been performed on a MALDI-TOF mass spectrometer Autoflex III Bruker Daltonics. The polymers have been dissolved in methanol P.A in a concentration of 10 mg mL^{-1} and alpha-cyano-4-hydroxycinnamic acid (HCCA, 10 mg mL^{-1}) was used as die and dissolved in a solution of 50% acetonitrile and 0.3% trifluoroacetic acid.

TEM (Transmission Electronic Microscopy) imagens have been obtained using a FEI equipment, Morgagni 268D, acceleration voltage of 40-100 kV, point resolution 0.45 nm, line resolution 0.34 nm, magnification of up to 180,000 X, camera CCD.

2.1. Synthesis of glycerol carbonate

Glycerol Carbonate (GC) was obtained as described by Rokicki et al.[16]. In a reaction flask, propane-1,2,3-triol (GLY) (80.10 g, 0.870 mol) has put with dimethyl carbonate (234.9 g, 2.61 mol) and K_2CO_3 as catalyst (3.6 g, 26.1 mmol). The reaction has been performed under reflux and magnetic stirring for 3 hours at 75°C. The crude product has filtered over an ion exchange resin (Amberlit IR 120) to remove the catalyst. Then, the product has been placed into rotaevaporator to remove the methanol. The monomer has been stored in a desiccator. Yield: 94%.

2.2 Synthesis of polymers (HPG)

The polymers have been synthesized by ring opening multibranched polymerization using a procedure described by Rokicki et al, with some modifications[16]. Briefly, 1,1,1-tris(hydroxymethyl)propane (TMP) or glycerol (GLY) have been used as core initiator in synthesis of hyperbranched and highly branched polymers through deprotonation with sodium methoxide at 1:3 molar ratio for 2 h at 25ºC. After, the monomer GC, in a molar ratio of 12:1 (GC/core), was slowly added for 6 h, at 150°C. Then, the mixture remained under stirring and heating for 24 hours. After cooling, the mixture has been filtered through Amberlit IR 120 and the solvent was evaporated by reduced pressure at 60°C. The same method was used with propylene carbonate. Four polymers have been obtained and labeled as: PGLYGC, PGLYPC, PTMPGC and PTMPPC, Fig. 1.

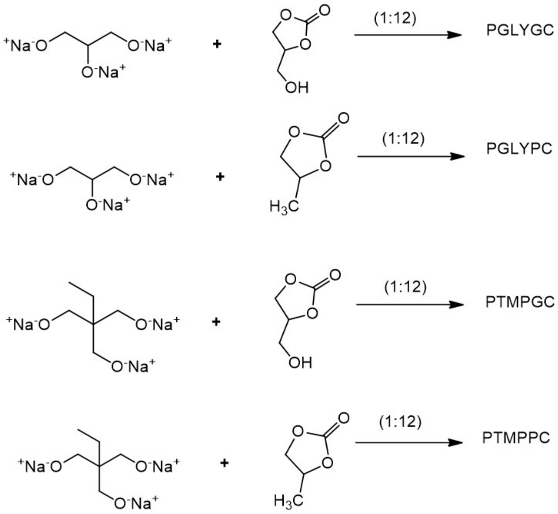

Figure 1. Reaction representation of the obtained polymers with respective core and monomers in the ratio 1:12

3. Results and Discussion

3.1 Polymers synthesis

The infrared technique was used to monitor the polymerization reaction until it was no longer observed the presence of carbonyl groups in 1784 cm^{-1} of GC and in 1796 cm^{-1} of PC monomers. Fig. 2(a) suggests the formation of polymers due to the stretching band elimination of the C=O group. Additionally, it was observed a band, Fig. 2(b), corresponding to a stretching of CH_2-O- ether linkage in the region between 1044-1040 cm^{-1}, confirming the success in obtaining the polymer[17,18].

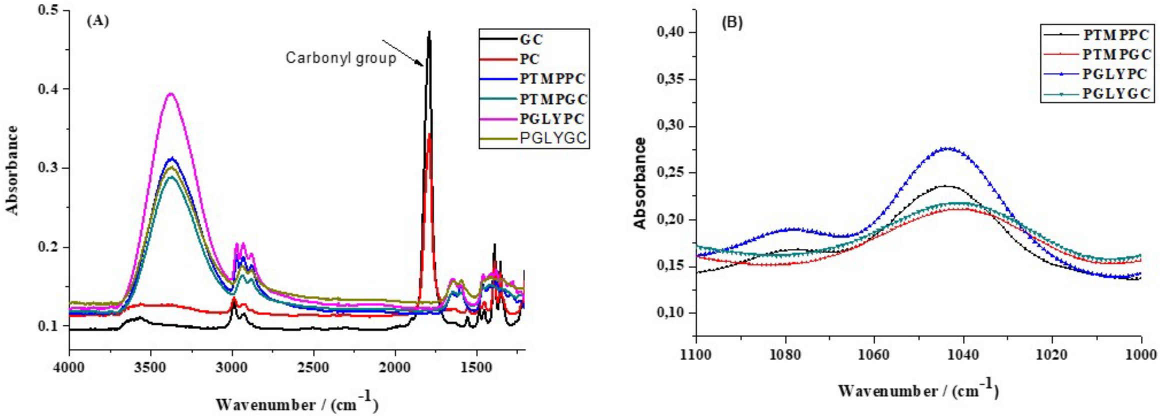

Figure 2. (A) GC, PC, PTMPPC, PTMPGC, PGLYPC and PGLYGC infrared spectra; (B) PTMPPC, PTMPGC, PGLYPC, and PGLYGC infrared spectra in the CH2-O- ethers linkages

3.2 Hyperbranched and highly branched units

AB_2-type monomers as GC have two OH active sites that make the three-dimensional polymerization architecture. Among the chain-growth possibilities, five units of GC branches are known, dendritic (D) monomeric unit, two linear units ($L_{1,3}$ and $L_{1,4}$) with one hydroxyl unreacted group, and two terminal groups ($T_{1,2}$ and $T_{1,3}$) with two free OH groups[16], Fig. 3. However, such units may be favoured over others depending on the polymer synthesis method[19,20].

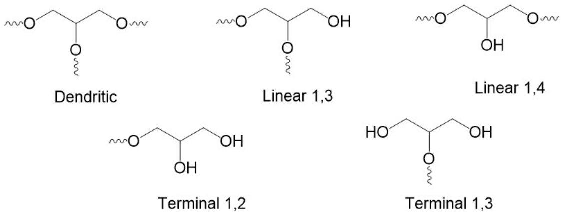

Figure 3. Structural variations of glycerol carbonate monomer

Propylene Carbonate is classified as AB_1-type monomer, since it has only one OH active site to polymerize. Thus, the AB_1-type monomer is not classified as potentially active monomer for the synthesis of hyperbranched polymers, because it is not possible to obtain polymers with three-dimensional structures from such monomers[21]. In this case, only two possibilities are accepted, first is the linear PC (L) monomeric unit, which reacts completely to promote the increase of the polymer chain, and the terminal unit (T) when the polymer growth is finished, Fig. 4. However, the core based on AB_2 initiator enables 3D growth, ensuring a highly branched aliphatic polymer, which justifies their characteristic as a viscous liquid, similarly to a hyperbranched polymer, and can be used for the same medicinal purposes, such as drug delivery, for example, and as conductor compounds with specific properties[22].

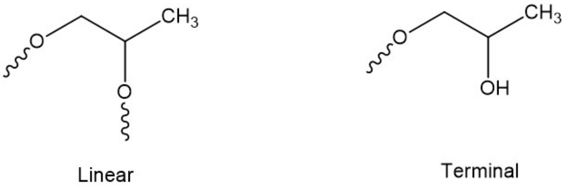

Figure 4. Representation units of PC monomers variations.

3.3. NMR data analysis

NMR technique has been used as a fundamental tool in the analysis of all branch possibility, theoretical molecular weight, degree of branching and the length of the dendritic, linear and terminal units. The proposed structures based on NMR data have shown in Fig. 5. All NMR spectra are available at the supplementary material.

HPG labeled PTMPGC has already described in literature[16,19,23,24], using a different synthetic route and less harmful due to the substitution of glycidol as monomer. ^1H NMR spectrum of PTMPGC shows the signals of TPM core in δ 0.75, 1.17 and 3.15 of methyl group H-1, methylene group H-2 and oxymethylene group H-4, respectively, Fig. S1. It is also possible to see signals at δ 3.70-3.20 of a standard of high complexity of polyglycerol, and δ 4.47 of OH terminals and linear groups. ^{13}C NMR spectrum shows signals of TMP core at δ 7.92 of methyl group (C-1), 21.76 of methylene group (C-2), 43.81 of quaternary carbon (C-3) and 62.28 of oxymethylene group (C-4), Fig. S2[16,19].

^1H NMR spectrum of PTMPPC shows signals at δ 0.74 (H-1, triplet), 1.16 (H-2, quintet) and 3.24 (H-4, singlet) which confirms the TMP incorporation. Besides, the monomer PC signals are observed at δ 0.96 (H-7, doublet), 3.15-3.24 (H-5, double doublet) and 3.54 (H-6, quintet), the signals at δ 4.51-4.56 represents the terminal OH group and 4.32 to secondary OH group, Fig. S3. ^{13}C NMR spectrum shows signals at δ 7.84, 21.73, 43.74, 62.31 of TMP core, and at δ 21.73 of CH_3 group of PC, Fig. S4.

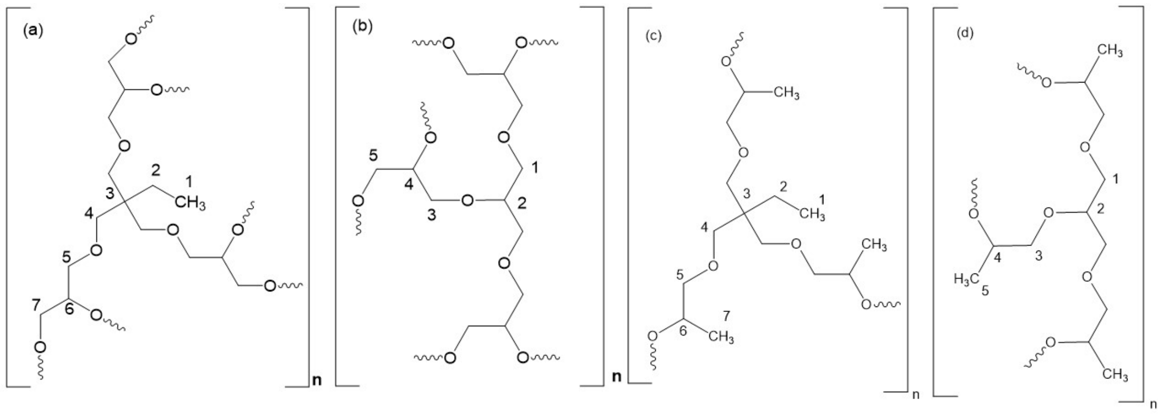

Figure 5. Proposed structures for (a) PTMPGC, (b) PGLYGC, (c) PTMPPC and (d) PGLYPC

The polymer PGLYGC and PGLYCP were obtained and characterized using the same NMR techniques. However, the core was glycerol sodium salt. The ^{1}H NMR spectrum of PGLYGC shows signals at δ 3.25-3.36 (double quartet) of oxymethylene group (H-1, H-3, H-5), δ 3.41 of oxymethynic group (H-2, H-4) and δ 4.47 of OH terminal and linear units, Fig. S5. The ^{13}C NMR spectrum presented two signals at δ 63.47 and 72.89 of oxymethylene and oxymethynic groups, respectively, which is characteristic of a polyglycerol[25], Fig. S6.

^{1}H NMR spectrum of PGLYPC shows signals at δ 0.96 (H-5, CH_3 group of PC), δ 3.16-3.33 of oxymethynic and oxymethylene groups corresponding to GLY core and at δ 3.54 (CH group of PC), and δ 4.54 of hydroxyl group, Fig. S7. ^{13}C NMR spectrum shows signals at δ 20.04 of CH_3 group, δ 63.25 and δ 72.63 corresponding to CH_2 and CH groups of GLY, Fig. S8. The signals at δ 67.40-67.58 are an overlap of CH and CH_2 groups of PC.

The identification of D, L and T units was possible with Inverse Gated and DEPT 135 techniques, Table 1. The assignments is based on two assumptions: first, accepting the degree of branching (DB) ranging from 0.4 to 0.8 calculated on Inverse Gated spectra and equation 1; second, according to the interpretation of deshielding level of the GC variable unit along the polymer. The amount of $L_{1,3}$ units is greater than of $L_{1,2}$ in the monomer GC, since the carbon 6, of the proposed structure for this polymer, is less reactive than carbon 7. Similarly, the $T_{2,3}$ units are present in larger amount than $T_{1,3}$, since $T_{1,3}$ units are connected by carbon 6, which is less probable. Fig. S9 shows the spectra of PTMPGC.

DEPT 135 spectrum of PGLYGC, Fig. S10, exhibits some similarities to the PTMPGC polymer due to the monomer being the same, consequently, the structural variations have no significant differences.

The assignments of PTMPPC and PGLYPC, Fig. S11 and S12, have made from deshielding level variable units along the polymer together with spectral data on the initiator/core unit (TMP and GLY) and propyl carbonate.

Table 1. NMR shifts of dendritic, linear, terminal units (CH and CH_2) for PTMPGC, PGLYGC, PTMPPC and PGLYPC analyzed by DEPT 135 and Inverse Gated

Units	PTMPGC	PGLYGC	PTMPPC	PGLYPC
$CH_{(D)}$	70.93	70.92		
$CH_{2(D)}$	63.49	63.47		
CH ($L_{1,3}$)	70.92	*		
CH_2 ($L_{1,3}$)	73.32	*		
CH ($L_{1,4}$)	72.92	72.88		
CH ($T_{1,4}$)	*	67.65		
CH ($T_{1,2}$)	71.86	70.90		
CH ($T_{1,2}$)	71.86	70.90		
CH ($T_{1,3}$)	71.86	*		
CH_2 ($T_{1,3}$)	66.23	73.26		
$CH_{3(L)}$			20.25	20.21
$CH_{3(T)}$			20.30	20.24
$CH_{2(GLY,TMP)}$			62.31	63.42
$CH_{2(L)}$			67.62	67.61
$CH_{(L)}$			67.63	67.68
$CH_{2(T)}$			67.64	70.90
$CH_{(T)}$			67.63	70.73
$CH_{(GLY)}$				72.84

* No assigned signals.

The signal at δ 67.63 observed in DEPT 135 spectrum of PTMPPC is an overlap of CH_2-CH, which occurs due to structural variation of PC along the growing chain of the polymer, where the OH group bonded to the CH or CH_2 group. This modification occurs because the environment is highly oxidant and this makes the signals to mix and form an single signal since its polymerization becomes highly random which ensures similar chemical environments[21].

The Inverse Gated NMR technique has used to estimate the molecular weight and calculate the degree of branched (DB) of the polymers. The spectra are exhibited in the supplementary material, Fig. S13, S14, S15, S16. The equation 1 has been used to calculate the DB of polymers[18,26,27].

$$\mathrm{DB} = \frac{\mathrm{D}+\mathrm{T}}{\mathrm{D}+\mathrm{L}+\mathrm{T}} \tag{1}$$

The DB to PTMPGC and PGLYGC were 0.667 and 0.669, respectively. According to Frey et al.[28], the value of DB to hyperbranched polymer around 0.6 means an very oxidant environment on polymer growth. Therefore, the values found to PTMPGC and PGLYGC are consistent considering the presence of sodium methoxide ionizing agent in the deprotonation step of the core/initiator (GLY), which provided an ionizing environment for hydroxyl of the monomer CG, making them more reactive. The Inverse Gated spectra of PTMPPC and PGLYPC have not provided the value of DB because the PC is an AB_1-type monomer, thus it is impossible to obtain three-dimensional structures.

The molecular weights have been estimated through relationships between core/monomer, Table 2.

Table 2. Estimative of molecular weights of polymers by NMR *Inverse gated*

Polymer	Relationship Core/Monomer	Estimative of Molecular Weight
PTMPGC	1/13.58	1149.5
PGLYGC	1.95/4.21	-
PTMPPC	1/17.81	1167.3
PGLYPC	1/21	1351.1

It was not possible to estimate the average molecular weight of the PGLYCG polymer by the Inverse Gated technique because the spectrum showed only two signals corresponding to CH and CH_2, and it was not possible to obtain the relation between them. The ratio CH/CH_2 was 1.95/4.20, which confirms the structure of the polymer as a polyglycerol without differentiating between core and monomer. However, the molecular weight is not different from the other polymers synthesized in this work, due to the similar characteristics and results. The literature described that hyperbranched polymers have molecular weights 1000 to 8000 $g.mol^{-1}$ [29].

3.4. MALDI-TOF characterization of the hyperbranched and highly branched polymers

The MALDI-TOF analysis allows the identification of fragmentations end groups, their series and molecular mass, Fig. 6. The MALDI-TOF spectra of PTMPGC shows a series of 5 peaks which correspond to a molecular mass of glycerol (92 $g.mol^{-1}$), Fig. 6(a). Moreover, the difference between the base peaks of each series exhibits a fragmentation of m/z 212 $g.mol^{-1}$ assigned to two GC monomer units bonded by carbonyl group (C=O). Besides, it has been observed the presence of peak/z 44 $g.mol^{-1}$ that corresponds to ionization technique of MALDI-TOF fragmentation.

The PGLYGC spectrum shows five peaks series with a molecular end group m/z 74 $g.mol^{-1}$ corresponding to the glycidol unit formation from the GC, initiated by the ionization MALDI-TOF technique, Fig. 6(b). The PTMPPC spectrum shows a 5 peaks series with a molecular end group of m/z 76 $g.mol^{-1}$ of propylene carbonate unit. The m/z 18 $g.mol^{-1}$ represents the H_2O molecule, absorbed from the environment, Fig. 6(c).

The PGLYPC, Fig. 6(d) spectrum shows a 5-peak series with a molecular leaving group of m/z 76 $g.mol^{-1}$ of PC monomer. It is also possible to see the fragmentation of m/z 44 $g.mol^{-1}$ of CO_2. All the MALDI-TOF-MS results corroborate with the predictions made in the Inverse Gated analysis.

The MALDI-TOF technique allows us to calculate the number average molecular weight (Mn), weight average molecular weight (Mw), polidispersity (PDI), and degree of polymerisation (nn) of polymers. The calculations were made according to the equations 2, 3, 4, 5[30] and Mn, Mw and PDI values are shown in Table 3.

$$\overline{M_n} = \frac{\sum m_i}{\sum N_i} = \frac{\sum N_i m_i}{\sum N_i} \tag{2}$$

$$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum m_i M_i}{\sum m_i} \tag{3}$$

$$PDI = \frac{M_w}{M_n} \tag{4}$$

$$n_n = \frac{\overline{M_n}}{\overline{m}}; \quad n_w = \frac{\overline{M_w}}{\overline{m}} \tag{5}$$

Where, "Mn" means the number average molecular weight, "Ni" corresponding an intensity of "Mi" peak, "Mi" is the number of chains with equal molar mass, "Mw" means average molecular weight, "PDI" is the polydispersity index, "Nn" is the degree of polymerisation and "m" corresponding to mero molar mass.

The molar mass calculated by MALDI-TOF is very similar from the measured by Inverse Gated Technique, and they are in accordance to the molar mass described in the literature to hyperbranched polyglycerols[31]. In addition, this technique allows to calculate the molar mass of PGLYGC. When the polymer has a great molecules size variation, the polydispersity is greater than 1, and when the chain sizes

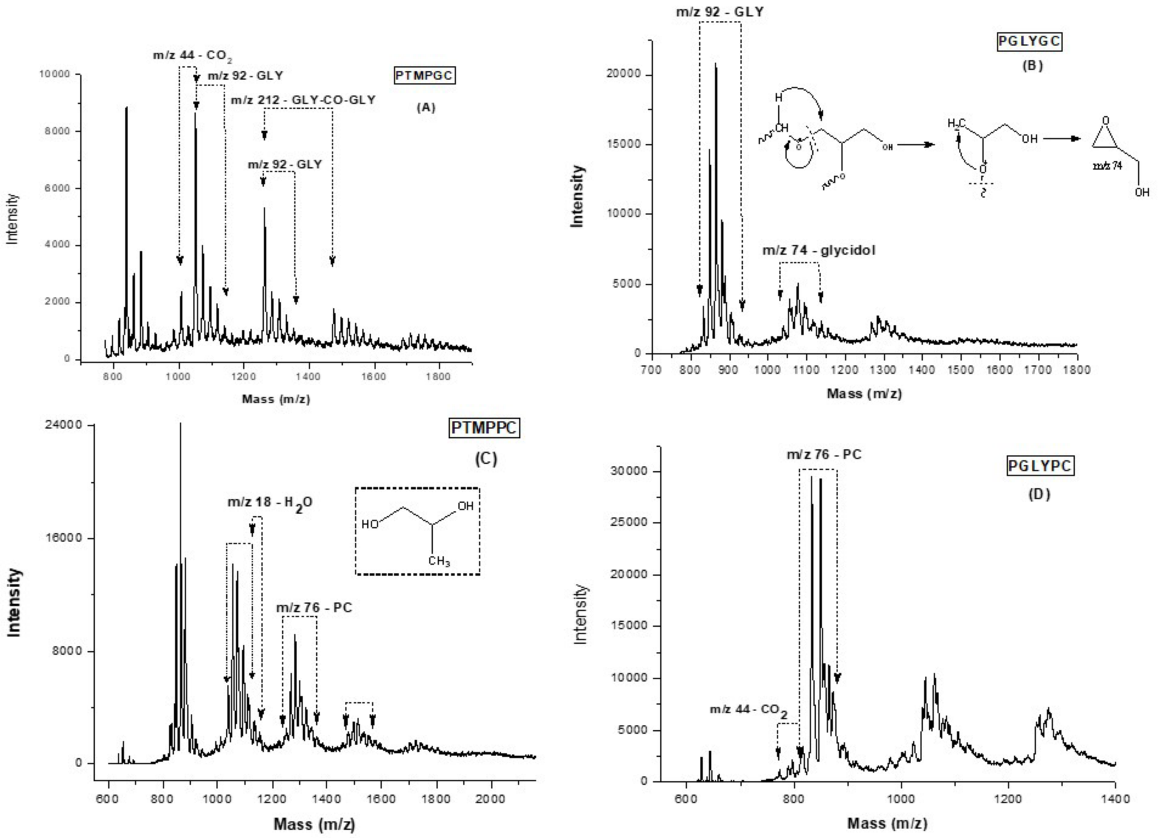

Figure 6. MALDI-TOF-MS spectra for (a) PTMPGC, (b) PGLYGC, (c) PTMPPC and (d) PGLYPC with their fragmentations, polymer series, leaving groups and fragmentation mechanism

Table 3. Mn, Mw, PDI and nn of polymers by MALDI-TOF spectra

Polymer	M_n	M_w	PDI	n_n
PTMPGC	1157.71	1238.86	1.070	13,001
PGLYGC	993.980	1027.551	1.033	11.168
PTMPPC	1143.175	1215.683	1.063	15.450
PGLYPC	1007.783	1045.124	1.037	13.620

are close, the polydispersity is about 1. In this work the polymers have a polydispersity close to one, therefore they have a chain size very close. We can explain this fact due to the method used to obtain the branched Polymer. The monomer was added slowly, and due to low concentration of monomer in the reaction medium, this creates a "controlled environment" for orderly growth of hyperbranched Polymer. Other authors described the synthesis of polyglycerols with PDI range from 1.1 to 1.5, and a molecular mass varying from 1.25 to 6.5 kDa. Moreover, the polymers synthesized in this paper presented a low molecular mass in comparison to the literature, the low value of PDI is justified by this factor also, because the lower molecular mass, the smaller is the possibility to form more dispersed chains[25].

3.5. Morphology of Hyperbranched Polymers

TEM images of PGLYGC and PTMPGC show spherical structures, Fig. 7. There is a dark nucleus and some branches around this nucleus. The image of PTPCGC is very clear on showing such branches. The histogram of PGLYGC shows particles ranging from 40 to 120 nm. However, the highest concentration of size is around 90 nm.

The PTMPGC shows particles ranging into two size blocks. In the first block, the particles range from 210 to 270 nm, and the second block the particles range from 300 to 360 nm. The highest sizes concentration is around 250 nm. These sizes are considered large nanoparticles, however for compounds that may be used for drugs delivery, a size up to 300 nm is not so problematic.

3.6. Mechanism of polymerization

Polymerization of AB_2-type monomer, as glycidol, follows a ROMBP anionic polymerization - ring opening multibranched polymerization, Fig. 8. Generally, the polymerization is initiated by an alkali metal alkoxide and an alcohol as initiatior/core. Alcohol unit partially deprotonated,

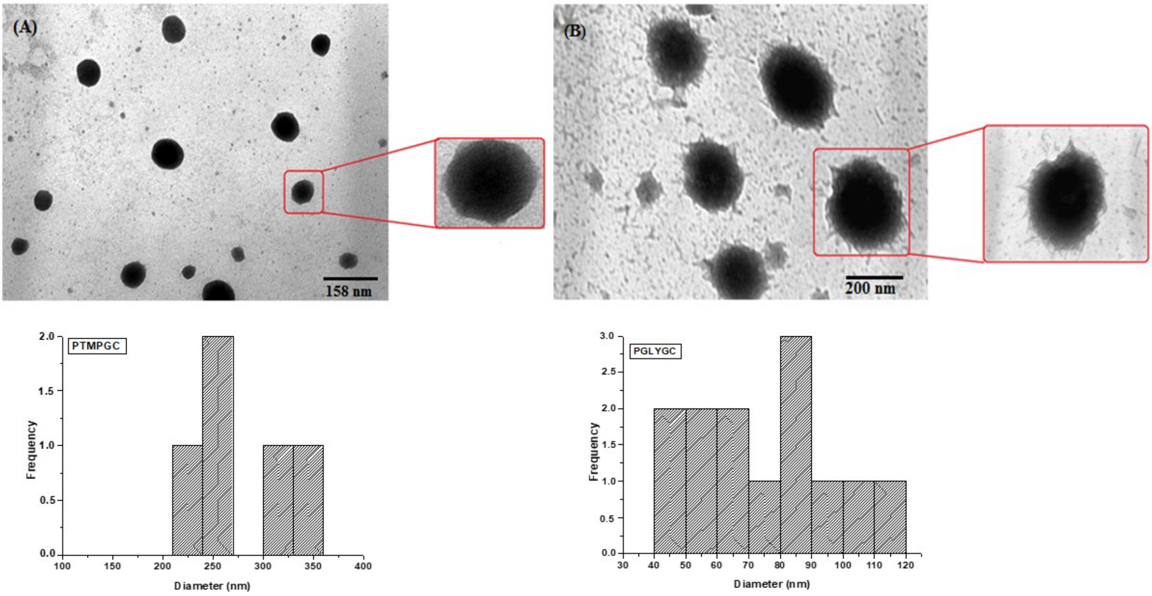

Figure 7. TEM Imagens of PGLYGC (A) and PTMCGC (B) with histograms.

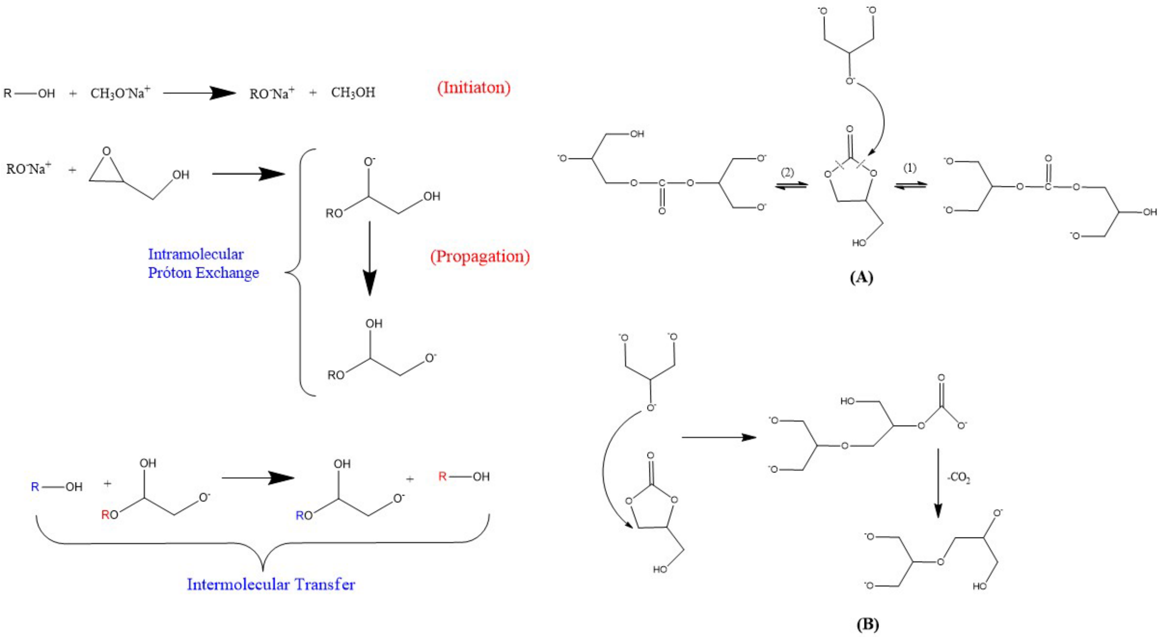

Figure 8. Mechanism of the anionic Polymerization of AB_2-type monomer (glycidol). (a) Carbonyl carbon atom attacked. (b) Alkyl carbon atom attacked.

are used, as they allow to control the concentration of active sites in polymerization. The literature showed that only 10% of the hydroxyl group deprotonate is enough to initiate the polymerization process. This control leads to the growth of all chain ends, as well as the control of molecular weight and narrowing of the polydispersity[25].

The next step (propagation), the alkoxide initiator reacts with the epoxide ring on its unsubstituted end group and generates a secondary alkoxide. The proton exchange in epoxide polymerization reaction occurs very fast between secondary and primary alkoxides and all chain end can grow simultaneously, resulting in a branched structure[26].

The proton exchange occurs via intra as well as intermolecular and leads to simultaneous growth of all hydroxyl group present in the system. As the polymerization reaction proceeds, the concentration of active species (hydroxyl end group) decreases. The incorporation of a glycidol monomer generates a new hydroxyl group representing a dormant

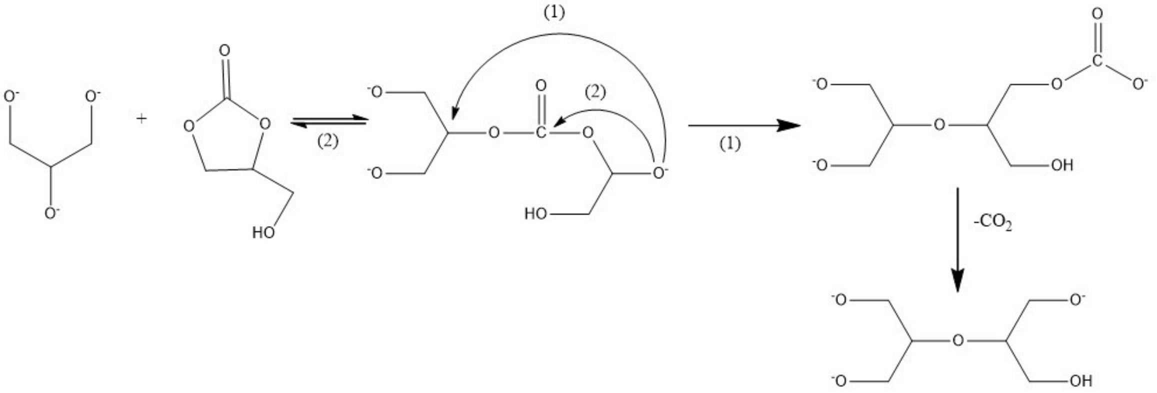

Figure 9. Mechanism of anionic polymerization of carbonate and alcohol (Glycerol)

chain end. The termination step of polymerization occurs by neutralization, and the polymer (polyglycerol) is obtained as a transparent, viscous liquid.

Pawlowski and Rokicki described that the polymerization mechanism of the carbonates (AB_2-type monomers), and an alcohol partially deprotonated, occurs by two pathways[31], Fig. 8a and 8b.

First, the carbonyl carbon atom is attacked by alkoxide group forming a linear carbonate. Second, the alkyl carbon atom is attacked by alkoxide group forming an ether linkage with a CO_2 elimination.

The first case is favoured kinetically, over the methylene group attack. However, the carbonyl group attack is reversible, while the methylene group attack is not, due to the rapid decarboxylation of terminal carbonate group as shown in Fig. 8b. Frey at al.[28] describe that in anionic polymerizations of glycidol, intra and intermolecular reaction may occur. Rokicki et al.[16] have shown that this phenomenon also occurs in the anionic polymerization of carbonates. The methylene group attack forms a secondary ether unit, with carbon dioxide liberation. According to this mechanism two primary hydroxyl group is formed by proton exchange reaction, Fig. 9.

In polymerization of glycidol the intermolecular reaction generates two kinds of ether units, secondary-primary or primary-primary. The primary alkoxide attacks via intramolecular the carbon atom of methylene group, and secondary-primary ether units are formed, Fig. 9. The same ether unit is observed in carbonate reaction, Fig. 8.

4. Conclusion

The hyperbranched polyglycerol using core-starting glycerol salt and glycerol carbonate was successfully synthesized. It is noteworthy that this polymer less harmful synthetic route had not been previously described in the literature. Furthermore, polymers using TMP and GLY salts as core starting and propyl carbonate as AB_1-type monomer have been synthesized. Those polymers were not described in the literature. The polymers structures were proposed by NMR techniques as well as their molecular weights. The degree of branching DB found to PTMPGC and PGLYGC were within the values described in the literature to hyperbranched polymers. MALDI-TOF have confirmed the structure proposed to polymers due the fragmentations at m/z=92 (glycerol), m/z= 76 (propyl carbonate), m/z=74 (glycidol) and m/z=44 (CO_2). In addition, MALDI-TOF enables the calculation of Mn, Mw and PDI of the polymers and the result did not differ much from that found when the NMR Inverse Gated technique was used. The importance of these polymers comes from huge potential for various purposes including drugs carriers. Then this is the next step that our research group has been working on and some good results have been found.

5. Acknowledgments

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Supplementary material

The following online material is available for this article:

Figure S1. ^{1}H NMR (DMSO-d6, 400 MHz) of PTMPGC.

Figure S2. ^{13}C NMR (DMSO-d6, 100 MHz) of PTMPGC.

Figure S3. ^{1}H NMR (DMSO-d6, 400 MHz) of PTMPPC.

Figure S4. ^{13}C NMR (DMSO-d6, 100 MHz) of PTMPPC.

Figure S5. ^{1}H NMR (DMSO-d6, 400 MHz) of PGLYGC.

Figure S6. ^{13}C NMR (DMSO-d6, 100 MHz) of PGLYGC.

Figure S7. ^{1}H NMR (DMSO-d6, 400 MHz) of PGLYPC.

Figure S8. ^{13}C NMR (DMSO-d6, 100 MHz) of PGLYPC.

Figure S9. DEPT 135 NMR (DMSO-d6, 100 MHz) of dendritic, linear and terminal units for PTMPGC.

Figure S10. DEPT 135 NMR (DMSO-d6, 100 MHz) of dendritic, linear and terminal units for PGLYGC.

Figure S11. DEPT 135 NMR (DMSO-d6, 100 MHz) of PTMPPC.

Figure S12. DEPT 135 NMR (DMSO-d6, 100 MHz) of PGLYPC.

Figure S13. Inverse Gated NMR expanded spectrum (DMSO-d6, 100 MHz) of dendritic, linear and terminal units for PTMPGC.

Figure S14. Inverse Gated NMR expanded spectrum (DMSO-d6, 100 MHz) of dendritic, linear and terminal units for PGLYGC.

Figure S15. Inverse Gated NMR (DMSO-d6, 100 MHz) of PTMPPC.

Figure S16. Inverse Gated NMR (DMSO-d6, 100 MHz) of PGLYPC.