Asian Journal of Chemistry; Vol. 24, No. 8 (2012), 3339-3346

ASIAN JOURNAL OF CHEMISTRY

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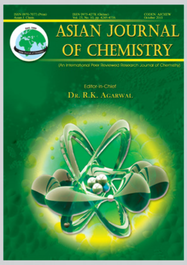


An Improved Understanding of the Influence of the Initiation Step on the Propylene Oxide Anionic Ring Open Polymerization

GABRIEL CENDEJAS, CÉSAR. A. FLORES*, FELIPE ARREGUÍN, ARISTEO ESTRADA, EUGENIO A. FLORES and FLAVIO S. VÁZQUEZ

Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, México D.F.

*Corresponding author: Fax: +52 55 91756239; Tel: +52 55 91758269, 5591756664; E-mail: caflores@imp.mx

(*Received*: 18 May 2011; *Accepted*: 1 March 2012) AJC-11139

The influence of the choice of three aliphatic and one aromatic potassium glycols as initiators on the bulk propylene oxide polymerization was investigated simultaneously by both theoretical and experimental methods. Special focus was made to elucidate the effect of the initiator on the final polypropylene oxide homopolymers polydispersity. The synthesized polymers were characterized through Fourier transform infrared and nuclear magnetic resonance. The polymer molecular weight is highly dependent on the starting initiator concentration, which was thoroughly established and systematically studied by size exclusion chromatography. Density functional theory calculations at B3LYP/-631G*d*(+) level were done in order to elucidate the experimental results. Furthermore, the transition states were obtained for all system, which led to understand the different growth patterns.

Key Words: Propylene oxide, Polyols, Initiator, Density functional theory.

INTRODUCTION

The polymerization of propylene oxide (PO) is a subject of continuous interest because polymers obtained this way may be employed as intermediates in the synthesis of block copolymers[1-5]. Indeed, poly(propylene oxides) (PPOs) can be reacted with isocyanates to make polyurethanes. Another application field is the employment of short chains of PPO bifunctionalized with -OH end groups, which are used as sites for growing poly(ethylene oxide) (PEO) segments. The obtained triblock copolymers, often denoted as PEO-PPO-PEO, are commercially known as Pluronic™ polyols (BASF); the equivalent ICI trade name is Synperonic™[6-8]. An adequate choice of the initiator employed to prepare the PPO, constituting the central segment of such a kind of triblock copolymers, is crucial because only a regular and symmetrical two side polymerization from the center can ensure a correct bifunctionalization with hydroxyls and low polydispersity of the polymer chains. Most common initiators used to prepare propylene oxide diols are salts obtained from the reaction between a glycol and a strong base of an alkaline metal like potassium. Once the PEO-PPO-PEO is formed, the hydrophilic/lipophilic balance will also be affected by the chemical structure of the initiator placed in the middle of the PPO hydrophobic segment[9,10]. In the specific field of petroleum demulsification, the efficiency of water separation from the crude oil is influenced by the initiator used to synthesize the triblock copolymer, due to the interactions between the hydrophobic center of the macromolecules and heavy compounds of the crude oil (resins and asphaltenes). The petroleum dehydration rate is also influenced by the surfactant molecular weight polydispersity, a factor determined also by the initiator.

Some attempts to understand the influence of the structure of some alkoxy and glycoxy initiators on the anionic ring opening polymerization of alkylene oxides, using experimental and theoretical methods, have been undertaken recently [4,11-15]. These studies revealed that more monodisperse polyethers may be obtained when aliphatic glycoxides are employed as initiators. In the present study, three aliphatic and one aromatic glycols were first employed to prepare a series of potassium glycolates and subsequently, assessed, as initiators of the bulk propylene oxide polymerization. The M_w, M_n average molecular weights and polydispersity (I) were calculated from size exclusion chromatography (SEC) measurements of the obtained polymers. Main focus was made on the influence of the initiator content on the final average molecular weights and polydispersity of the synthesized PPOs. The effect of the initiation step on the molecular features of the synthesized polymer chains was investigated exhaustively, by means of quantum chemical (QC) calculations, mainly by using the density functional theory with a B3LYP functional. These calculations has been taken into account the calculus of energy of each growing fragment, to observe the difference between an aliphatic and aromatic initiator. Furthermore, the transition states (TS) were obtained for the whole system, which led to understand the different propagation pathways. The contrast between the experimental and theoretical results leads to elucidating the complex propagation patterns entailed by the propylene oxide anionic ring open polymerization.

EXPERIMENTAL

(±)-Methyloxirane [propylene oxide (PO), Aldrich, 99 %], KOH (pellets, Fermont 99 %), ethylene glycol (EG, J.T. Baker, 99 %), butylene glycol (BG, J.T. Baker, 99 %), dipropylene-glycol (DPG, J.T. Baker, 99 %), Resorcinol (R, Sigma-Aldrich, 99 %), THF anhydrous (Mallinckrodt, 99.8), hexane (Sigma-Aldrich), methanol (Sigma-Aldrich) and polypropylene oxide standards (provider/supplier) were used as received with no additional purification.

Polymerization procedure

Synthesis of initiators: Preparation of di-potassium ethylene glycolate (DKEG), di-potassium butylene glycolate (DKBG), di-potassium di-propylene glycolate (DKPG) and di-potassium resorcinolate (DKR).

Each one of diol compounds (ethylene glycol, butylene glycol, dipropylene glycol and resorcinol), in different amounts, was dissolved in 80 mL of methanol and a calculated amount of potassium hydroxide was added. The resulting solution was heated at 80 ºC and stirred for 2 h, hence 1 mL of dry benzene was added and the solvents were removed under reduced pressure.

Polymerization process: The reactions were performed in a glass reactor (Parr) with digital stirring rate control, as well as pressure and temperature controls. The set up of the reactor consists of three fundamental steps. i) Filling the vessel with the starting mixture, consisting of initiator and monomer; ii) Drain and pressurization of the reactor with nitrogen to achieve an inert atmosphere and iii) Controlled heating during the reaction course. The initiator content was varied to obtain PPOs with different molecular weights. The polymerizations were carried out at 80 ºC. The reactions were terminated with a stoichiometric amount of a water solution of 85 % (v/v) phosphoric acid. Afterwards, the polymeric material was separated in the organic fraction by extraction with a solvent mixture containing 70 mL of hexane and 70 mL of bi-distilled water. The final conversions were determined by gravimetric measurement of non-volatile material.

Polymer characterization: Polymer analysis was performed by FTIR using a Brucker Tensor 27 Spectrometer, method: ATR, software: OPUS and NMR ^{1}H and ^{13}C in a Varian NMR spectrometer model Mercury-BB at 200 and 50 MHz respectively. Sample solutions were prepared for the ^{1}H and ^{13}C NMR measurements by dissolving the polymer sample in $CDCl_3$ as solvent. Chemical shifts are expressed in δ scale downfield from tetramethylsilane (TMS), the internal reference standard. The molecular weight distributions of polymer samples were determined by size exclusion chromatography, using an Agilent 1100 chromatograph consisting of a 5 µm column of Plegl and employing THF as eluent. The average molecular weights M_n, M_w and I were calculated from the SEC data. Calibration was made with a polystyrene standards kit.

Computational procedure: The structure was first optimized by using MM+ molecular modeling and semi-empirical PM3 method, which are implemented in the Hyperchem 6.0 software[16]. For these calculations a Polak-Ribiere conjugate gradient algorithm was employed, whereas the RMS gradient was of 0.0001 kcal/(Å mol). Afterwards, DFT calculations implemented in the Gaussian 98 program were performed[17]. Thus, the structure obtained was fully optimized at B3LYP/6-31G(*d*) level, following by a single-point calculations at B3LYP/6-31G+(*d*) level[18-20]. Diffused functions were used because better energy values were obtained for anionic species. The energy values were corrected by zero-point energy (ZPE) correction. Vibrational frequencies calculated ascertained the structure was stable (no imaginary frequencies). Transition states were reached employing the QST3 method[21]; then the resultant conformation was optimized using the TS key work at B3LYP/6-31G+(*d*) level. Finally, natural bond orbital (NBO) analyses were carried out using NBO 5.0, which is implemented in Gaussian 98.

RESULTS AND DISCUSSION

The polymerizations were performed with different compositions of di-potassium ethyleneglycolate (DKEG), di-potassium butylene glycolate (DKBG), di-potassium di-propylene glycolate (DKPG) and di-potassium resorcinolate (DKR). Results of these polymerizations are reported in Table-1 and Fig. 1. Very monodisperse chains, with a polydispersity index lower than 1.10, in a molecular weight interval between 920 and 2 800 Daltons were obtained when the polymerizations were started by DKEG. In contrast, a narrower interval of molecular weights (900 ≤ Mn ≤ 2000 Dalton) and less mono-disperse (I ≈ 1.11) polymer chains were synthesized using DKBG initiator). The propylene oxide polymerizations started with DKPG leading to obtaining olygomers with a mono-dispersity close to that of chains synthesized with DKBG, but with a higher rank of molecular weights (1 400 ≤ Mn ≤ 3 600 Daltons). Lowest conversions at the end of the polymerization period were detected for the polymerization initiated with DKPG. In contrast, higher conversions were measured in polymerization starting with DKEG.

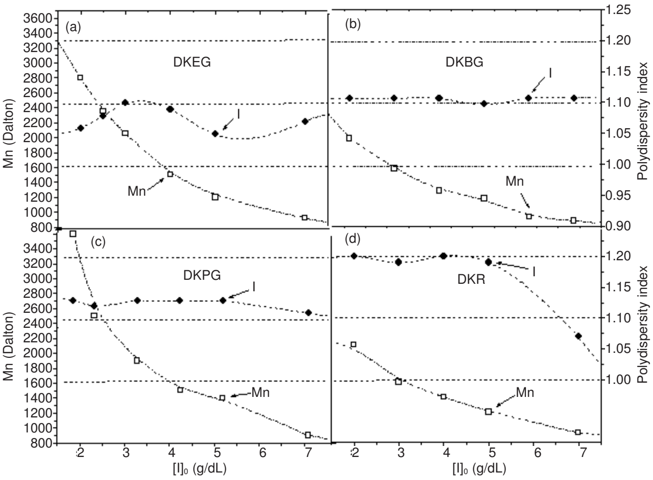
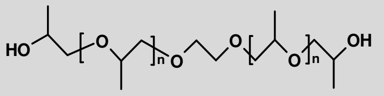
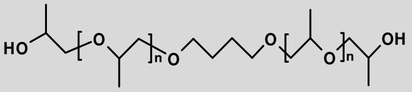
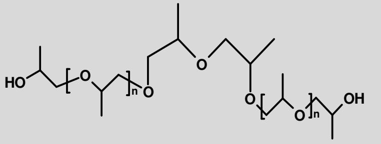
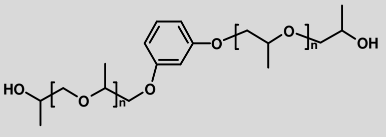


Fig. 1. Average molecular weight (Mn) and polydispersity index of PPOs synthesized using as initiators a) DKEG, b) DKPG, c) DKBG and d) DKR (T = 80º, reaction = 18 h)

TABLE-1
EXPERIMENTAL RESULTS OF THE BULK POLYMERIZATION OF PO INITIATED BY DIFFERENT GLYCOLS
(T= 70 °C, $t_{reaction}$ = 18 h, CONVERSION (*x*), WEIGHT AVERAGE MOLECULAR WEIGHT (M_w), NUMBER MOLECULAR AVERAGE WEIGHT (M_n) AND POLYDISPERSITY INDEX (I)

Polymer structure	 (PPO-DKEG-PPO)				Polymer structure	 PPO-DKBG-PPO			
[I] (g/dL)	x	M_n (Da)	M_w (Da)	I	[I] (g/dL)	x	M_n (Da)	M_w (Da)	I
2.0	0.44	2800	2968	1.06	2.0	0.25	2000	2220	1.11
2.5	0.77	2350	2538	1.08	3.0	0.70	1600	1776	1.11
3.0	0.83	2050	2255	1.10	4.0	0.71	1300	1443	1.11
4.0	0.87	1500	1635	1.09	5.0	0.82	1200	1320	1.10
5.0	0.90	1200	1260	1.05	6.0	0.83	950	1055	1.11
7.0	0.96	920	984	1.07	7.0	0.92	900	999	1.11
Polymer Structure	 PPO-DKPG-PPO				Polymer Structure	 PPO-DKR-PPO			
[I] (g/dL)	x	M_n (Da)	M_w (Da)	I	[I] (g/dL)	x	M_n (Da)	M_w (Da)	I
1.5	0.27	3600	4068	1.13	1.0	0.12	2200	2618	1.19
2.0	0.63	2500	2800	1.12	2.0	0.61	2100	2520	1.20
3.0	0.79	1900	2147	1.13	3.0	0.67	1600	1904	1.19
4.0	0.82	1500	1695	1.13	4.0	0.77	1400	1680	1.20
5.0	0.89	1400	1582	1.13	5.0	0.76	1200	1428	1.19

The initiation performance of this sequence of aliphatic glycolates, shows certain regularity. However, a different behaviour was detected in the propylene oxide polymerizations starting by DKR. The oligomers growth from these aromatic initiators were more polydisperse in size (I ≈ 1.20) and showed a very narrow molecular weight (Mn) interval, between just 1200 and 2200 Daltons. The conversions performed with this initiator, at the same period of time, were less than those detected when an aliphatic glycol was employed to initiate the polymerization.

The initiator performance of these series of glycoxides may be clearly correlated to their dissolution easiness in the propylene oxide. A considerable dissolution of initiator salt in the monomer could be detected when using aliphatic glycoxydes; observing an opposite behaviour for DKR. This aromatic compound enables a preliminary absorption of propylene oxide. For reaching an adequate dissolution in the monomer a continuous and powerful stirring is required. However, if the initiator solubility is an important parameter, which must be carefully surveyed, it will not explain completely the differences of molecular weight and polydispersity, exhibited by the different glycoxides. A theoretical chemical study is necessary to elucidate the diverse propagation patterns during the propylene oxide polymerization.

All synthesized polymers were characterized by FTIR. In the case of PPOs synthesized with aliphatic initiators (DKEG, DKBG and DKPG) the band of hydroxyl groups is located at 3500-3400 cm^{-1} region. These signals confirm the presence of the final hydroxyl groups at the ends of polymer chains. The signal corresponding to methyl and methylene groups could be observed at around 2950-2850 and the alkyl-substituted ether O-C characteristic band, at the interval of 1100-1050 cm^{-1}, indicating the polymerization reaction was performed (Fig. 2a). In the specific case of PPOs prepared with an aromatic initiator (DKR) some signals between 1600 and 1650 cm^{-1} were detected in the spectra (Fig. 2b), confirming the presence of an aromatic ring in the polymer backbone.

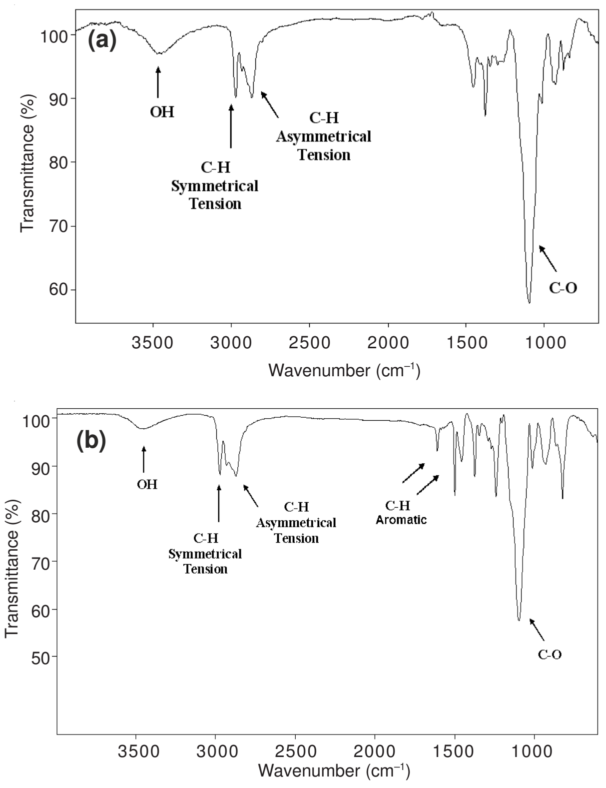
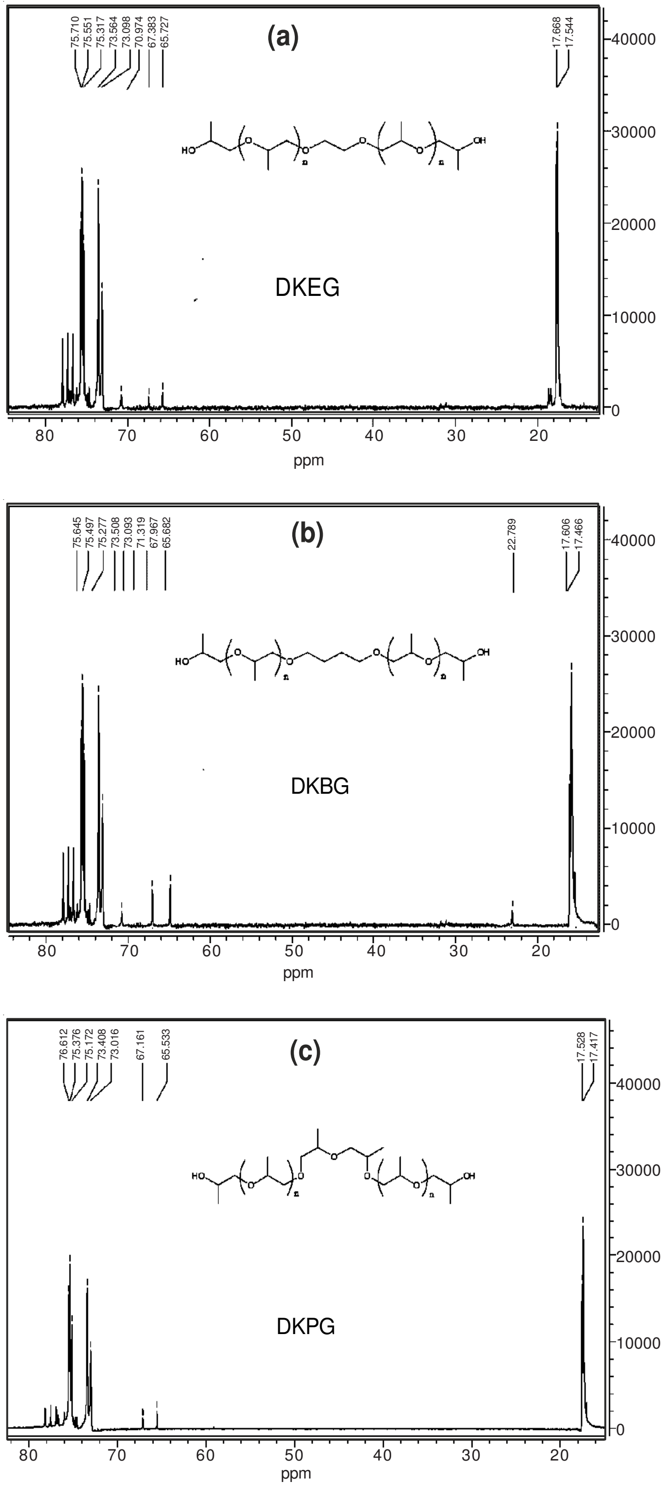


Fig. 2. FTIR spectra of PPOs synthesized by anionic bulk polymerization using as initiators: a) a series of aliphatic potassium glycolates (DKEG, DKPG and DKBG) and b) an aromatic potassium glycolate (DKR) as initiator, (T = 80°, treaction = 18 h)

The PPOs synthesized by anionic ring opening polymerization, using the formerly mentioned initiators were also characterized by ^{13}C NMR. The ^{13}C NMR spectra (Fig. 3) revealed that the peaks at 16.5-18 ppm may be assigned to the methyl carbons of polypropylene chain [-O-CH$_2$-CH(CH$_3$)-]; those around 65-70 ppm to carbon atoms bonded to hydroxyl terminal groups [HO-CH$_2$-CH(CH$_3$)-] and [HO-CH(CH$_3$)-CH$_2$-] in the polymer. In the case of signals around 73-77 ppm, they may be associated to either methylene or methine carbons attached to oxygen atom [-O-CH$_2$-CH(CH$_3$)-] and [-O-CH(CH$_3$)-CH$_2$-].



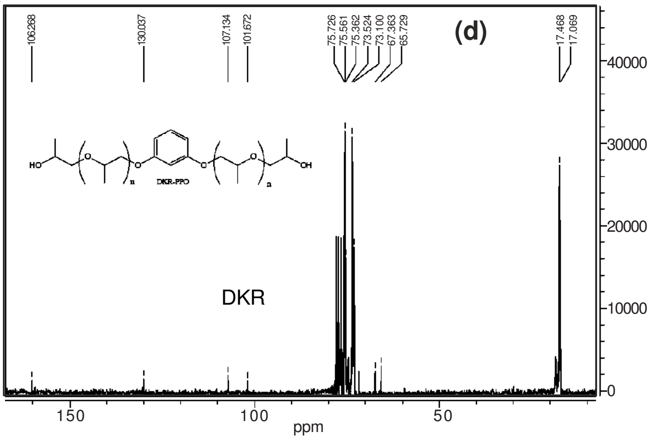


Fig. 3. ^{13}C NMR spectra of PPOs synthesized using a) DKEG, b) DKPG, c) DKBG and d) DKR as initiators

The ^{13}C NMR spectra of DKR (Fig. 3) at downfield showed several signals between 110-160 ppm zone; attributed to aromatic ring carbons[13]. Furthermore, in DKEG, DKBG, DKPG and DKR ^{13}C NMR spectra there were no signals due to monomer transfer.

Theoretical results: In order to explain the difference of polydispersity values experimentally observed, when aliphatic and aromatic initiators were used, a theoretical study was carried out at DFT level. The correlation was thereby taken into account, between the polydispersity and the theoretical energy values for several growth patterns. Four dianionic initiation systems were considered: a) ethylene glycolate (DKEG); b) butylene glycolate (DKBG); c) dipropylene glycolate (DKPG); and d) *m*-phenyl glycolate (DKR) (Fig. 4). DKEG and DKBG are lineal alkoxylates, whereas the DKPG is a branched glycolate, with an ether function in the structure. The terminal oxygen atoms are bonded to carbon atoms with different grade of substitution. DKR is an aromatic species with a *meta*-relationship among oxygen atoms.

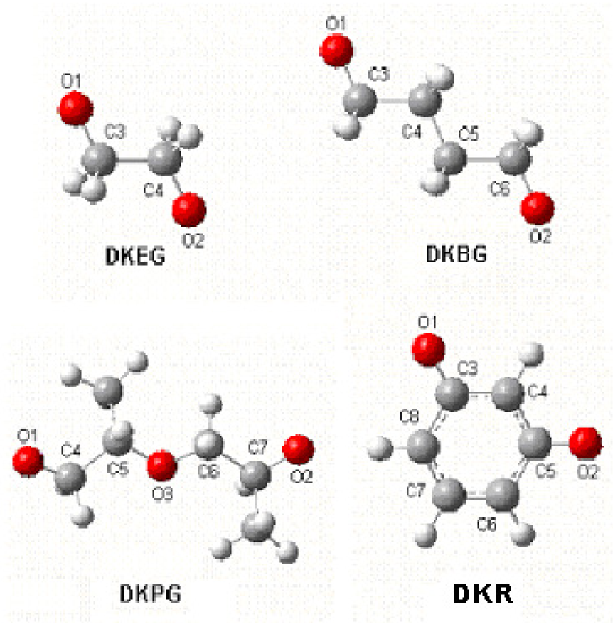


Fig. 4. Structure of the four dianionic initiation systems employed in this work: ethylene glycoxide, propylene glycoxide, butylene glycoxide and resorcinolate

We have reported the polymerization process of hydroxyl anion and ethoxy anion with propylene oxide[15]. It was observed that the addition *anti*, orientation regarding methyl group of propylene oxide, is preferred over the *syn* addition; which is a regioselective addition; thus only an *anti* addition was taken into account in this work. Furthermore, the nucleophilic attack (anionic oxygen atom from glycolate specie) to propylene oxide molecule, during the monomer activation (ring opening[21]), was exclusively over the carbon with the lowest substitution. This kind of attack is such as that observed in a substitution nucleophilic bimolecular (S_N2) reaction. Therefore, the propagation patterns could go two ways: a) a symmetrical growth, where two propylene oxide units are added to each side of the diglycolate molecule; and b) an unsymmetrical growth, where only one side of the glycolate is growing (Figs. 5-7).

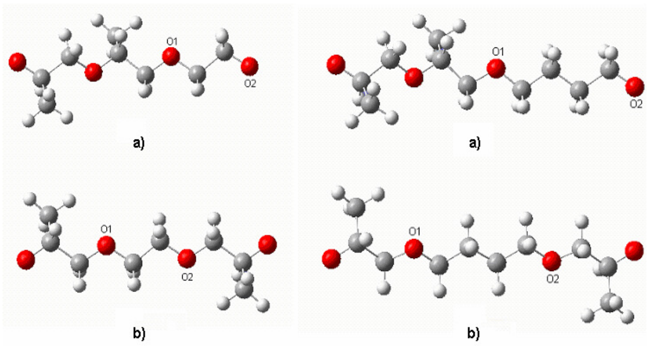


Fig. 5. a) Polymerization by one side (unsymmetrical grown) and b) by both sides (symmetrical grown) for DKEG and DKBG

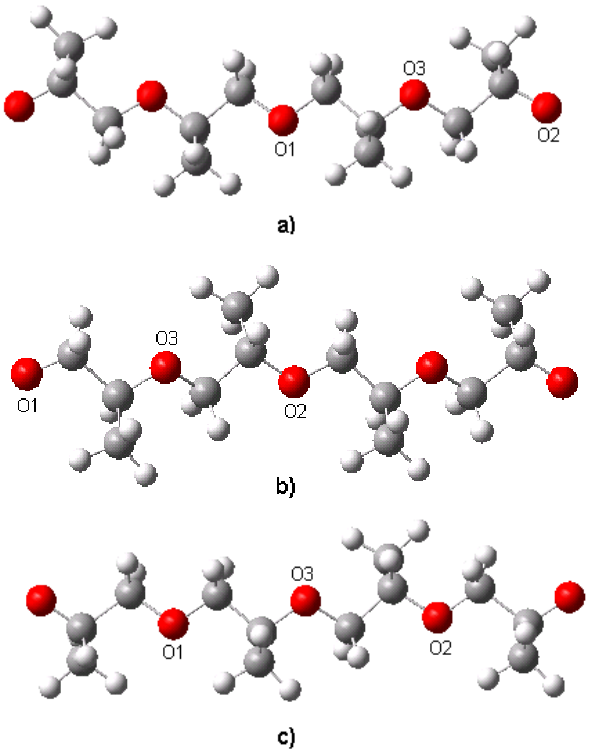


Fig. 6. Propagation patterns after the activation of PO by DKPG: a) unsymmetrical growth from the primary oxygen atom; b) unsymmetrical growth from the secondary oxygen atom; and c) polymerization from both sides (symmetrical growth)

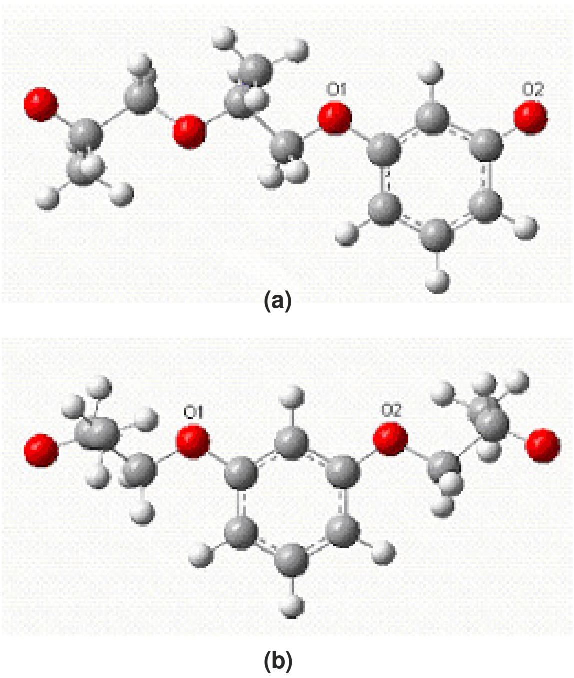


Fig. 7. a) Polymerization from one side (unsymmetrical growth) and b) from both sides (symmetrical growth) for DKR

The energy of each structure was obtained from the single-point calculations done at the B3LYP/6-31G+(d) level theory with the B3LYP/6-31G geometries. At this point, all energy values listed in the tables take into account the zero-point energy (ZPE) correction. Diffuse functions in single-point calculations were employed because for anionic systems, this function has an important effect over the energy value. Calculating anions with no diffuse functions generally overestimates mutual electron repulsion; it even gives false interactions of each electron. The calculations were performed in gas phase, as the polymerization reaction; mentioned above, was a solventless reaction (bulk polymerization).

Reckoning to the geometric parameters of the optimized structure, the dihedral angles of the fragments O1-C3-C4-O2 for DKEG and O1-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-O2 for DKBG, show an alternate conformation (angle close to 180º), corresponding to the conformer of minimum energy. Moreover, the O-C bond length value in both compounds is approximately 1.36 Å. Regarding DKPG, the presence of methyl groups and ether function provokes a distortion of the alternate conformation (Table-2). For DKR the O-C bond length is 1.2794 Å, this reduction is due to an electronic delocalization of oxygen atom with the aromatic ring.

TABLE-2
GEOMETRICAL PARAMETERS FOR DKPG INITIATOR

Bond Length (Å)		Dihedral Angle (°)	
O1–C4	1.3317	O1–C4–C5–O3	179.82
O2–C7	1.3317	C4–C5–O3–C6	–165.53
O3–C5	1.4305	C5–O3–C6–C7	174.83
O3–C6	1.4302	O3–C6–C7–O2	175.91

Atomic charges of nucleophilic oxygen atoms for all compounds were obtained by using Mulliken population analysis (MPA), electrostatic potential analysis (ESP) and

TABLE-3
POPULATION ANALYSIS FOR DKEG, DKBG, DKPG AND DKR INITIATION SYSTEMS

Compound	Population analysis					
	MPA		ESP		NPA	
DKEG	–0.8110	–0.8110	–1.1974	–1.1862	–0.5213	–0.5212
DKBG	–0.7722	–0.7721	–1.2331	–1.2364	–0.5056	–0.5055
DKPG	–0.7458[a]	–0.7004[b]	–1.1015[a]	–1.1717[b]	–0.4942[a]	–0.4869[b]
DKR	–0.7755	–0.7754	–0.9826	–0.9381	–0.4339	–0.4339

[a]Oxygen atom bonded to one primary carbon. [b]Oxygen atom bonded to one secondary carbon

natural population analysis (NPA) (Table-3). It is known that Mulliken population analysis is undoubtedly sensitive to basis set, particularly when this one is enlarged to a higher accuracy; whereas electrostatic potential analysis and natural population analysis are not affected by the basis set employed. Oxygen atoms in DKR show the lower negative values, due to the strong electronic delocalization with the aromatic ring by resonance effect.

Tables 4-7 list energy values, with ZPE correction, obtained from single-point calculation at B3LYP/6-31G+(*d*) level for the addition of one to ten propylene oxide molecule. Regarding the DKEG and DKBG systems (Tables 3 and 4), a symmetrical growth is preferred over an unsymmetrical one; wherein the Es-Eu value ranges between 0.0054 and 0.0091 hartrees (3.4 and 5.7 kcal/mol) for DKEG, 0.0037 and 0.0085 hartrees (2.3 and 5.3 kcal/mol) for DKBG.

TABLE-4
ENERGY VALUES FOR DKEG INITIATION SYSTEM

PO Units	Energy (Hartrees)		
	Unsymmetrical growing (Eu)	Symmetrical growing (Es)	Es–Eu
1	–421.9717	-	-
2	–615.0640	–615.0712	–0.0072
4	–1001.2147	–1001.2201	–0.0054
6	–1387.3494	–1387.3565	–0.0071
8	–1773.4800	–1773.4867	–0.0067
10	–2159.6097	–2159.6188	–0.0091

TABLE-5
ENERGY VALUES FOR DKBG INITIATION SYSTEM

PO Units	Energy (Hartrees)		
	Unsymmetrical growing (Eu)	Symmetrical growing (Es)	Es–Eu
1	–500.5655	-	-
2	–693.6479	–693.6559	–0.0080
4	–1079.7923	–1079.7999	–0.0076
6	–1465.9264	–1465.9349	–0.0085
8	–1852.0595	–1852.0632	–0.0037
10	–2238.1843	–2238.1889	–0.0046

TABLE-6
ENERGY VALUES FOR DKPG INITIATION SYSTEM

PO Units	Energy (Hartrees)		
	A1	A2	A3
1	-	–654.0962	–654.0936
2	–847.1161	–847.1165	–847.1166
4	–1233.1397	–1233.1397	–1233.1401
6	–1619.1536	–1619.1541	–1619.1547
8	–2005.1589	–2005.1648	–2005.1655
10	–2391.9670	–2391.9672	–2391.9674

TABLE-7
ENERGY VALUES FOR DKR INITIATION SYSTEM

PO Units	Energy (Hartrees)		
	A1	A2	A3
1	–574.4438	-	-
2	–767.5284	–767.4968	–0.0317
4	–1153.6767	–1153.6430	–0.0337
6	–1539.8085	–1539.7759	–0.0326
8	–1925.9382	–1925.8974	–0.0409
10	–231.0779	–2312.0339	–0.0439

For the DKPG initiation system, the two anionic oxygen atoms have different chemical environment (Fig. 8). O1 atom is bonded to a primary carbon atom, whereas O2 atom is bonded to a secondary carbon atom. This way, three polymerization ways were proposed for this dianion: a) a symmetrical propagation (A1 system); b) a growth from O1 atom (A2 system) and c) a growth from O2 atom (A3 system) (Fig. 5). As mentioned above, the opening of the epoxide molecule behaves like an S_N2 reaction. Therefore, comparing the two anionic oxygen atoms, the O1 atom should be more reactive toward propylene oxide unit than the O2 atom, as O1 atom is sterically less hindered than the O2 atom. After the first propylene oxide addition, the A2 system is 1.6 kcal/mol more stable than A3. However, after the second addition of propylene oxide (Table-6), the A3 system is more stable than A1 and A2 systems, wherein the energy values ranging between 0.25 to 0.69 and 0.06 to 0.44 kcal/mol respectively; this difference could be due to steric factors.

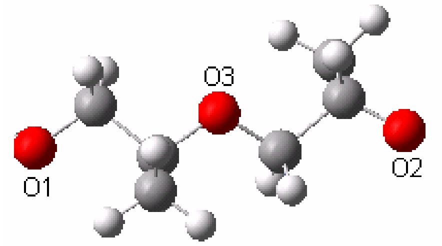


Fig. 8. Oxygen atoms labeled for DKPG initiator

Regarding aromatic glycoxyde (DKR, Table-7) an unsymmetrical propagation is preferred to a symmetrical one, ranging between -0.0317 and -0.0439 hartrees, resulting into a meaningful energetic difference. This preference is mainly due to a strong electronic delocalization of the unshared electron pair of the oxygen atom with the electronic cloud of the aromatic ring. From the second order perturbation theory analysis of Fock matrix in NBO basis, the $n_O \rightarrow \pi^*_{Ca\text{-}Cb}$ and $n_O \rightarrow \pi^*_{Ca\text{-}Cc}$ for both oxygen atoms in DKR were of 7.08 and 7.31 kcal/mol, respectively. Resonance effects are therefore, so important in the reaction mechanism, causing a preferential way in the growth of the chain. These results agree with the low conversions, narrow range of molecular weights and high polydispersities, observed during the synthesis.

Summing up, symmetrical growths are preferred in aliphatic compounds, where only electronic effects of non-bonding, as hindrance steric, drive the propagation pattern. Meanwhile, in the case of the polymerization initiated by an aromatic compound, the unsymmetrical one is preferred. Here, mainly, resonance effects drive the propagation pattern along the propylene oxide polymerization. Therefore, electronic delocalization provokes high polydispersity values. Other parameters that could be related with the polydispersity value are the dipolar moment and the GAP (difference of EHOMO-ELUMO). These parameters were obtained for the five systems adding ten propylene oxide units. This amount of propylene oxide units added corresponds to a symmetrical growth for aliphatic initiators and unsymmetrical growth for the aromatic initiator. Tables 8 and 9 show the dipolar moment values and GAP values, respectively. In both tables, the values increased in the following order: DKEG < DKBG < DKPG < DKR; therefore, the higher dipolar moment and GAP values, the lower conversion and higher polydispersity values.

TABLE-8
DIPOLAR MOMENT VALUES IN DEBYES
OF CHAINS WITH TEN PO UNITS

PO units	Systems			
	DKEG	DKBG	DKPG	DKR
10	2.3441	2.9520	3.2638	6.1899

TABLE-9
GAP VALUES IN HARTREES OF CHAINS WITH TEN PO UNITS

PO units	Systems			
	DKEG	DKBG	DKPG	DKR
10	0.12088	0.12187	0.12243	0.12203

The transition states (TS) were obtained from the first propylene oxide addition (activation step) with the four initiators studied in this work. The transition structures and their geometric parameters were determined by using the QST3 method. Transition structures were confirmed by calculating the vibrational frequencies.

Tables 10 and 11 lists the geometric parameters obtained for the transition states of DKEG and DKBG initiation systems. In both cases, the attack of the nucleophilic oxygen is close to 180º. However, the formation of the bond O1-C8 provoked a quasi-eclipsed conformation for the substituents in the C4-C5 bond; the dihedral angle was 13.66º, provoking a change in the dihedral angle value of the C4-C5-C6-O2 fragment regarding the optimized structure.

TABLE-10
GEOMETRICAL PARAMETERS OF THE TS
FOR DKEG INITIATION SYSTEM

Bond length (Å)		Dihedral angle (°)	
O1–C6	1.4520	O1–C6–C7–O5	−167.68
O5–C6	2.3885	O1–C3–C4–O2	176.69

TABLE-11
GEOMETRICAL PARAMETERS OF THE TS
FOR DKBG INITIATION SYSTEM

Bond length (Å)		Dihedral angle (°)	
O1–C8	1.4414	O1–C3–C4vC5	179.20
O7–C8	2.4038	C4–C5–C6–O2	−167.34
		C3–C4–C5–C6	−104.59
		C4–C3–O1–C8	−79.87
		O1–C8–C9–O7	174.96

About DKPG initiation species, two transition states were calculated considering the first propylene oxide addition: a) when the primary oxygen atom (TS1) acts as the nucleophile and b) when the secondary oxygen atom (TS2) acts as the nucleophile. The TS1 structure is 3.5 kcal/mol, more stable than the TS2 structure (Tables 12 and 13), being the steric hindrance who provokes this energy difference. Hence, there is a slightly preferable selectivity of primary oxygen atom for reacting first with the propylene oxide molecule. Regarding to the O-C bond length of epoxide moiety that should be broken, there is no significant variation if the oxygen nucleophilic is primary or secondary.

TABLE-12
GEOMETRICAL PARAMETERS OF THE TS FOR DKPG
SYSTEM, INITIATED BY A PRIMARY OXYGEN ATOM (TS1)

Bond length (Å)		Dihedral angle (°)	
O1–C9	1.4520	O1–C9–C10–O8	178.68
O8–C9	2.3910	O1–C4–C5–O3	−175.42
		C4–O1–C9–C10	−108.29

TABLE-13
GEOMETRICAL PARAMETERS OF THE TS
FOR DKPG SYSTEM, INITIATED BY A
SECONDARY OXYGEN ATOM (TS2)

Bond length (Å)		Dihedral angle (°)	
O2–C9	1.4463	O2–C9–C10–O8	−176.10
O8–C9	2.3920	O2–C7–C6–O3	178.56
		C7–O2–C9–C10	−168.62

Table-14 shows the geometrical parameters for the transitions state of DKR initiation system. For DKR system the bond values of the oxygen nucleophilic and carbon atom electrophilic are quite similar to those of aliphatic compounds. However, when the nucleophile is more bulky, the C7-O9 bond is shorter than the other systems; whereas the O1-C7 bond value increased approximately 2.1 Å, due to the steric hindrance. Hence, this transition state is affected by the bulk of the nucleophilic moiety.

TABLE-14
GEOMETRICAL PARAMETERS OF THE TS
FOR DKR INITIATION SYSTEM

Bond length (Å)		Dihedral angle (°)	
O1–C7	1.4533	C3–C2–O1–C7	39.22
O1–C2	1.3819	C2–O1–C7–C8	−132.14
C7–O9	2.3936	O1–C7–C8–O9	179.69

To sum up the transition state discussion, Fig. 9 shows the TS structure for all the systems, whereas the thermochemical parameters for all the systems are listed in Table-15. Comparing the DG^1 values for aliphatic compounds, it shows the following order DKBG < DKEG < DKPG; in this case the order of DKBG and DKEG are interchanged compared with the experimental conversion values. Indeed, the lowest conversion is reached with propylene glycolates, intermediate with butylene glycolates and the highest using ethylene glycolate as initiator. Furthermore, in DKPG the energy of the system is 0.94 kcal/mol lower when the primary oxygen atom is the nucleophile, than when the secondary oxygen atom acts as the nucleophile, which is in agreement with result above obtained. Regarding aromatic compounds, DKR shows a lower value than DKBG, which could be due to the stability by resonance effect.

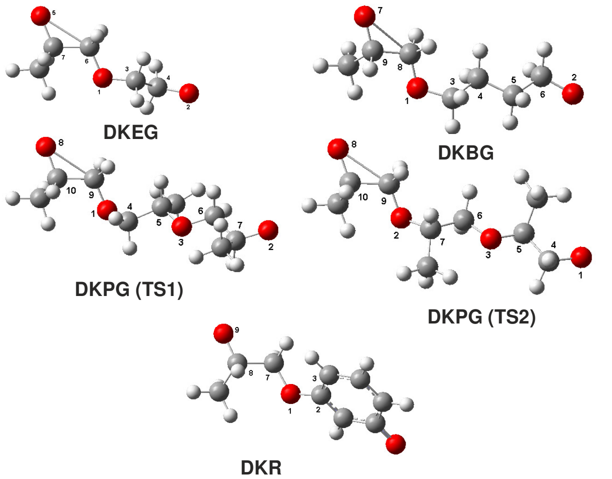


Fig. 9. Transition state structure for all compounds during activation step

TABLE-15
THERMOCHEMICAL PARAMETERS FOR ALL INITIATORS

Initiator	Thermochemical parameters (kcal/mol)		
	ΔH_r	ΔG_r	$\Delta G^{\neq}$
DKEG	63.76	48.89	5.40
DKBG	150.36	134.41	2.69
DKPG^a	41.51	24.68	6.77
DKPG^b	37.13	21.74	7.74
DKR	40.66	26.28	2.25

Conclusion

One of the most important parameters controlling the final conversions, average molecular weights and polydispersity of PPO chains synthezized by anionic ring opening polymerization, is the choice of the initiator. Poly(propylene oxide) chains develop from two active points on a segment constituted by a glycoxide. A fast simultaneous monomer attack from these two points leads to a regular chain growth, which will be translated by low polydispersities, relative high molecular weights and conversions. A good solubilization of the glycoxide in the propylene oxide monomer at the beginning of the reaction is also required to induce the required epoxy ring opening in the monomer. A decreasing performance of the initiator, in terms of conversion, molecular weight and monodispersity was observed in the aliphatic series DKEG > DKBG > DKPG. Thermochemical parameters, ΔH_r, ΔG_r and $\Delta G^{\#}$ values showed that an activation reaction with DKBG and DKEG initiators is preferred to that with DKPG initiator, which is in agreement with the final conversion values experimentally determined. In addition, higher polydisperse PPOs, with small molecular weights and at low conversions, were synthesized using as polymerization starter DKR. DFT calculations, revealed that resonance effect in this aromatic initiator, due to a strong electronic delocalization of the unshared electron, pair the oxygen atom with the electronic cloud of the aromatic ring, $n_O \rightarrow \pi^*_{C-C}$, has an important role in the low monodispersities and molecular weight values. Therefore, this delocalization provoked an unsymmetrical propagation. Though, when aliphatic initiators are used to start polymerization, a symmetrical propagation is preferred, being the steric hindrance that drives the growth pattern.

Finally, in order to decrease the polydispersity of PPO chains synthesized from an aromatic initiator, a fragment could be introduced in the aromatic ring, such as CH_2, avoiding the resonance effect, but maintaining a high electronic density (aromatic ring). The presence of an aromatic initiator in the polymer chain is very important for emulsification and dehydrating applications in the petroleum industry, because of the interaction between the chemical product and the heavy compounds of the crude oil (asphaltenes).

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