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Novel initiators for the synthesis of propylene oxide oligomers by anionic ring opening polymerization

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Abstract

A series of potassium alcoholates was obtained from the reaction between KOH and ethylene glycol, resorcinol, 4,4′-bisphenol A, 4,4′-(1,3 phenylenediisopropylidene)-bisphenol, 4,4′-sulfonyldiphenol. These salts were employed to initiate the anionic ring opening polymerization of propylene oxide (PO). The molecular weight distribution of the propylene oxide oligomers prepared by this method and the initiator structure were correlated. These oligomers were characterized through Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR) spectroscopies and size exclusion chromatography (SEC). It was found that the molecular weight and polydispersity of the synthesized poly(propylene oxide) (PPO) is highly dependant on the initiator structure and solubility in the reactive medium. The oligomers obtained using di-potassium resorcinolate exhibited a molecular weight distribution more polydisperse than that of PO oligomers synthesized by means of di-potassium ethylene glycolate. In the case of the PO polymerizations started by the potassium salts of 4,4′-bisphenol A, 4,4′-(1,3 phenylenediisopropylidene)-bisphenol and 4,4′-sulfonyldiphenol, the oligomer chains showed very broad molecular weight distributions. In general, lower solubility and augmentation of the polymer polydispersity were observed when the number of aromatic rings in the initiator structure increased. The experimental results were contrasted with those obtained from quantum chemical semiempirical calculations at AM1 level. The peculiar behavior exhibited by the initiators with an aromatic structure could be explained in terms of different reactivities of the initiation sites. The theoretical studies revealed that the ring in the aromatic initiators promotes an unsymmetrical growing when the PPO chains are formed. In contrast, the identical reactivity of both initiation sites in the ethylene glycolate produces a symmetrical growing during the PO polymerization.

Keywords: Propylene oxide; Oligomers; Anionic ring opening polymerization (AROP); NMR; FTIR; SEC; Quantum semiempirical calculations; Initiator; Alkoxides

1. Introduction

Oligomers of poly(propylene oxide) are used for numerous applications and are bulk commodity materials [1]. They are prepared by anionic ring opening polymerization (AROP) [2], which can be initiated by an alkoxide. A correct choice of the initiator is very important because the chemical structure of this molecule has a strong influence on the final average molecular weight and chain polydispersity [3]. The initiator structure also plays a critical role in oligomer solubility in organic media [4,5]. Initiators with two active sites are particularly interesting because they are used as intermediates in the synthesis of triblock copolymers, with wide applications as surfactants.

Different di-potassium glycoxides, mainly with aromatic structures, have been used as initiators of the AROP of PO. In the specific case of petroleum industry products, this structure, incorporated into the polymer chain, improves the physicochemical interactions with wax or asphaltenic compounds in crude oil. In addition, the hydroxyl groups at the end of the chains may be employed as targets for an ulterior bifunctionalization with chemical groups, which contribute to improve their application as demulsifiers. On the other hand, the influence of the initiator structure on the molecular weight distribution of the oligomer chains has been thoroughly investigated [6,7]. The PO oligomers were synthesized by bulk polymerization in a batch reactor. The

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reactions between potassium hydroxide and a series of glycols were used to prepare the initiators. The procedure for synthesizing the initiators was adapted from that reported using glycerol [8,9]. The obtained materials were characterized by spectroscopic methods and size exclusion chromatography. This last technique made possible to obtain the chain length distributions. Afterwards, quantum calculations revealed different growing patterns produced by the initiators.

2. Materials and methods

2.1. Materials

(±)-Methyloxirane (propylene oxide (PO), Aldrich, 99%), KOH (pellets, Fermont 99%), ethylene glycol (J.T. Baker, 99%) resorcinol (Sigma-Aldrich, 99%), 4,4′-bisphenol A (Sigma-Aldrich 99%), 4,4′-(1,3 phenylenediisopropylidene)-bisphenol (Sigma-Aldrich 99%), 4,4′-sulfonyldiphenol (Sigma-Aldrich 98%), THF anhydrous (Mallinckrodt, 99.8), methanol (Sigma-Aldrich), hexane (Sigma-Aldrich) were used as received without additional purification.

2.2. Synthetic procedure of initiators

Preparation of di-potassium ethyleneglycolate (DKEG) and aromatic initiators, di-potassium resorcinolate (DKR), di-potassium 4,4′-bisphenolate A (DKB), di-potassium 4,4′-(1,3 phenylenediisopropylidene)-bisphenolate (DKPDIB), and 4,4′di-potassium sulfonyldiphenolate (DKS).

Each of these compounds (2 g) was dissolved in 80 mL of methanol and a stoichiometric amount of potassium hydroxide was added. The resultant solution was heated at 80 °C and stirred during 2 h, followed by addition of 1 mL of dry benzene, and the solvents were removed under reduced pressure. The products obtained (see Fig. 1) were characterized thoroughly by FTIR in order to confirm that the reactions were completed.

2.3. 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 consisted of three fundamental steps: (i) filling of 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. A constant amount of initiator (2 g) was introduced into the reactor containing 83 g of monomer. The polymerizations were carried out at a temperature of 80 °C. The stirring rate during the reaction was of 50 rpm. After a polymerization period of 16 h, the reactions were terminated with a stoichiometric amount of an aqueous solution of 85% (v/v) phosphoric acid in order to remove the residual potassium present in the polymer [10]. Afterwards, the polymeric material was separated from the organic phase by extraction with a solvent mixture of 70 mL of hexane and 70 mL of bidistilled water. The final conversions were determined by gravimetric measurement of non-volatiles fractions.

2.4. Characterization

Polymer characterization 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 (SEC) [11], using an Agilent 1100 Chromatograph consisting of a 5 μm column of Plegl and employing THF as eluent. The average number (M_n), weight (M_w) molecular weights and polydispersity index ($I = M_w/M_n$) were calculated from SEC data.

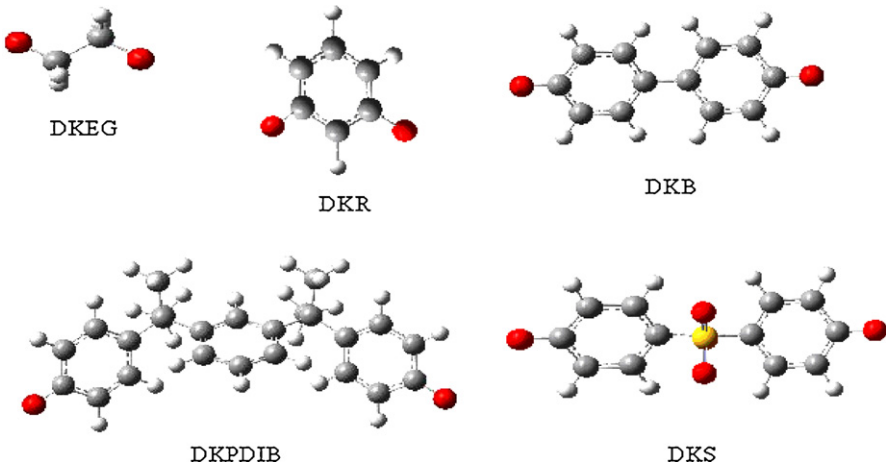

Fig. 1. Chemical structures of di-potassium glycolate (DKEG), di-potassium resorcinolate (DKR), di-potassium 4,4′-bisphenolate A (DKB), di-potassium 4,4′-(1,3 phenylenediisopropylidene)-bisphenolate (DKPDIB) and 4,4′di-potassium sulfonyldiphenolate (DKS).

Calibration was made with a polystyrene standards kit. The calibration with PS was checked by determining the average molecular weights and polydispersity index of a series of PPO standards furnished by Polymer laboratories™ (Mn = 580, 1270, 2960, 7200, 21,000, 50,400, 113,300, 325,000 and 696,500 g mol^{-1}).

2.5. Computational procedure

The Hyperchem software v. 6.0 was employed to run the calculations. Mechanical molecular calculations (MM) at MM+ level and semiempirical calculations at AM1 (Austin Method 1) level were performed Polar-Ribiere (conjugate gradient) algorithm and a root mean square (RMS) gradient of 0.01 kcal/(Å mol) was employed to reach the minimal energy structure.

3. Results and discussion

3.1. Experimental results

A series of PO polymerizations were performed to evaluate di-potassium ethyleneglycolate (DKEG), di-potassium resorcinolate (DKR), di-potassium 4,4′-bisphenolate A (DKB), di-potassium 4,4′-(1,3 phenylenediisopropylidene)-bisphenolate (DKPDIB) and 4,4′di-potassium sulfonyldiphenolate (DKS) as initiators. The structures of the obtained polymers are summarized in Fig. 2. A constant amount of initiator (2 g) was introduced into the reactor containing 83 g of monomer. The results of these polymerizations are shown in Table 1.

Table 1
Reaction time, conversion and average molecular weight of PPOs obtained by AROP at 80 °C using, di-potassium ethyleneglycolate (DKEG), di-potassium resorcinolate (DKR), di-potassium 4,4′-bisphenolate A (DKB), di-potassium 4,4′-(1,3 phenylenediisopropylidene)-bisphenolate (DKPDIB) and 4,4′di-potassium sulfonyldiphenolate (DKS) salts as initiators

Initiation system	Time (h)	Final conversion (%)	Mn (g mol^{-1})	*I*
DKEG	16	75	3100	1.10
DKR	16	63	2300	1.23
DKB	16	53	743	1.34
DKPDIB	16	56	1136	1.42
DKS	16	50	588	1.29

The DKEG achieved a high conversion, greater than that of the AROPs initiated with aromatic compounds. A very monodisperse distribution of the polymer chains was observed by SEC, which means that all the reactive centers were produced at the same time, and there was a very regular growing pattern of the chains during the propagation step of the reaction. The DKEG is easily dispersed in the reaction medium because it is a viscous

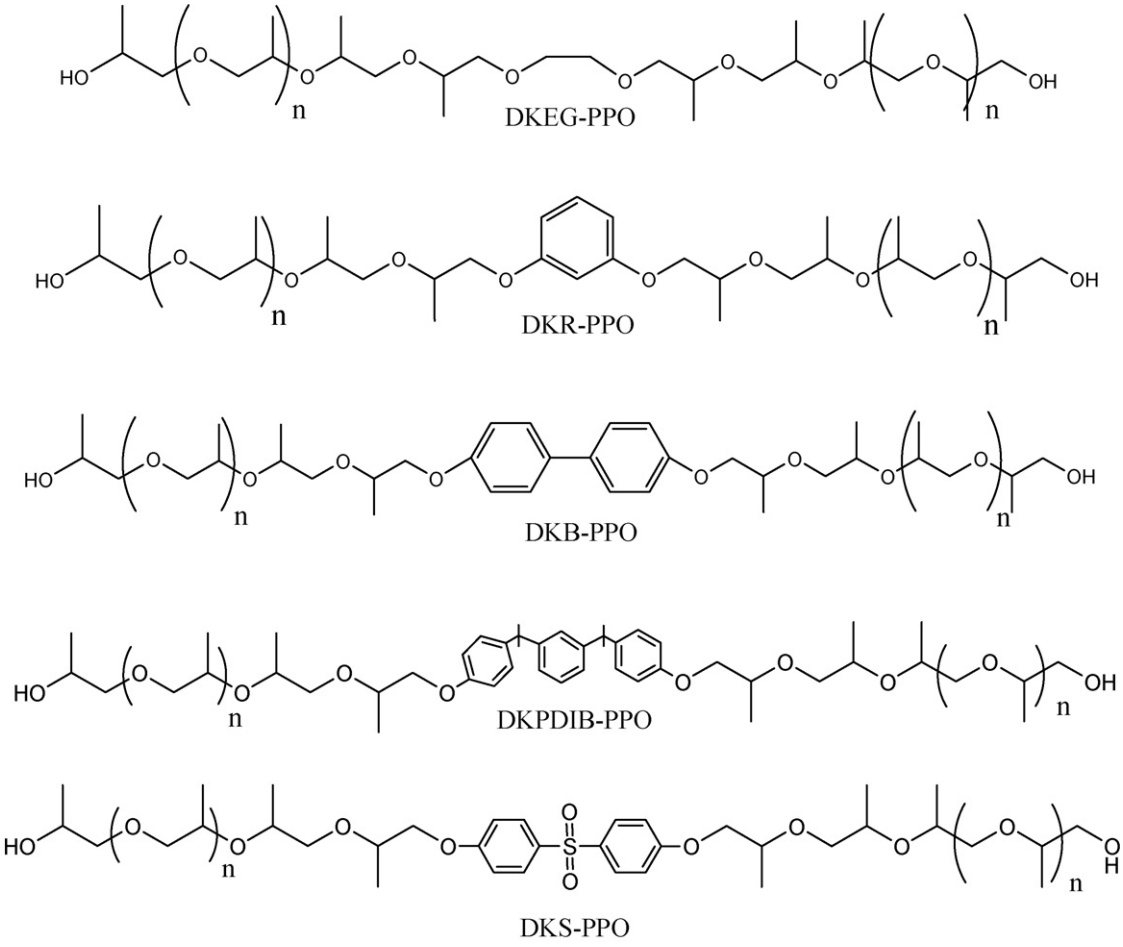

Fig. 2. Structures of PPOs synthesized by means of different glycolate initiators.

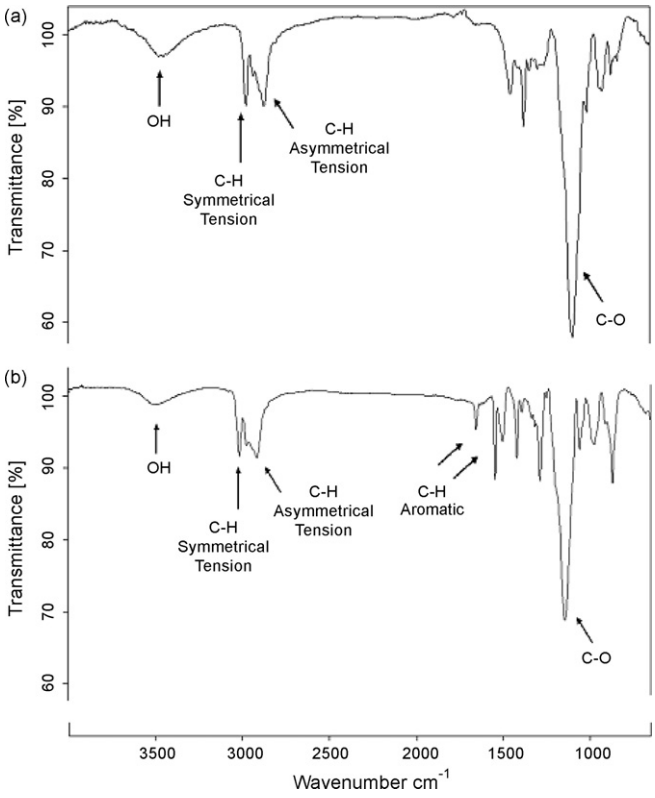

Fig. 3. FTIR spectra of PPO synthesized by anionic bulk polymerization initiated with: (a) DKEG and (b) DKR.

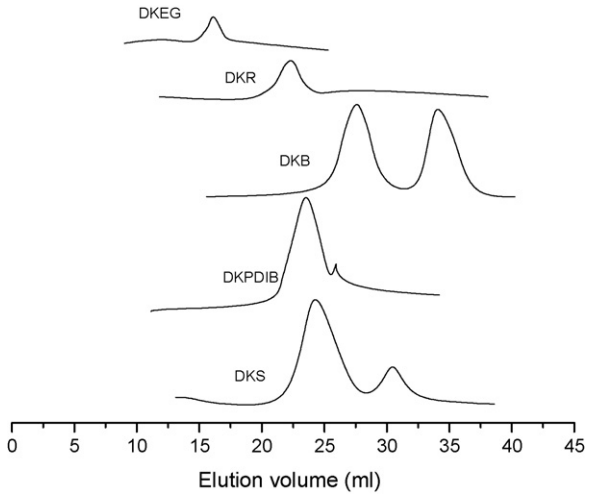

Fig. 4. Size exclusion chromatographs of PPOs synthesized by AROP initiated with DKEG, DKR, DKB, DKPDIB and DKS at $T = 80\ ^{\circ}C$.

liquid, in contrast to the aromatic initiators, which are solids. All the aromatic initiators were less efficient than the DKEG because of their lower solubility in the monomer. In addition, SEC measured more polydisperse polymer distributions. Among this initiator group, the most efficient was the DKR, since polymers prepared by means of this initiator showed low polydispersity and a conversion around 60%. Very polydisperse polymers were synthesized by means of the other aromatic glycolates, because one of the anionic reactive sites was stabilized by the resonance effect of the aromatic ring in the initiator structure during a first propagation step, and afterwards, the second reactive site is activated, as will be shown in Section 4.1 of this work.

4. Fourier transform infrared spectroscopy (FTIR)

All the synthesized polymers were characterized by FTIR, showing the alkyl-substituted ether C–O stretching characteristic band at the interval of 1090–1100 cm^{-1} that indicates that the polymerization reaction was performed. The characteristic band of hydroxyl groups appears about 3400–3500 cm^{-1}. This signal confirms the presence of hydroxyl groups in the polymer. The signals corresponding to methylene and methyl groups could be observed around 2850–2900 cm^{-1}. In the case of PPOs prepared with aromatic initiators, a range of signals between 1600 and 1650 cm^{-1} was detected in the spectra (see Fig. 3). This signals confirmed the incorporation of the aromatic structure in the polymer.

The PPOs prepared by anionic ring opening polymerization using the formerly mentioned initiators were characterized subsequently by ^{13}C NMR (see Table 2).

All these ^{13}C NMR spectra revealed that the peaks at 16.5–18 ppm may be assigned to the methyl carbons of poly(propylene oxide) 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 an oxygen atom [–O–CH_2–CH(CH_3)–] and [–O–CH(CH_3)–CH_2–]. The ^{13}C NMR spectra of the polymers containing aromatic structures showed at downfield several signals between 110 and 160 ppm zone; they were attributed to aromatic ring carbons.

As mentioned previously, low-average molecular weight and a narrow polymer distribution were determined by SEC when the PO polymerization was started with the salt of di-potassium ethyleneglycolate (DKEG). These results indicate that short

Table 2
^{13}C NMR shifts of PPOs synthesized by means of different glycolate initiators

	DKEG	DKR	DKB	DKPDIB	DKS
[–O–CH_2–CH(CH_3)–] and [HO–CH(CH_3)–CH_2–]	17.5, 17.7	17.1, 17.5	16.5, 16.8	16.9, 17.2	16.8, 17.1
[HO–CH_2–CH(CH_3)–] and [HO–CH(CH_3)–CH_2–]	65.7, 67.4	65.8, 67.3	65.3, 66.8	65.3, 66.8	65.4, 66.9
[–O–CH_2–CH(CH_3)–] and [–O–CH(CH_3)–CH_2–]	73.5, 75.7	73.7, 75.5	72.9, 74.2	74.2, 75.6	72.9, 74.7
Aromatic ring carbons	–	102.0, 107.1, 130.0, 160.3	114.5, 127.3, 133.1, 157.6	113.5, 126.9, 142.5, 159.2	115.6, 129.3, 136.5, 162.4
$(Ar)_2$–C–$(CH_3)_2$	–	–	–	41.1	–
$(Ar)_2$–C–$(CH_3)_2$	–	–	–	30.4	–

PPO chains were synthesized because a great number of initiation centers activated the monomer molecules during the early stages of the polymerization. The oligomers obtained using di-potassium resorcinolate exhibited a broader molecular weight distribution than that of PO oligomers synthesized by means of di-potassium ethylene glycolate. In the case of the PO polymerizations started by the potassium salts of 4,4′-bisphenol A, 4,4′-(1,3 phenylenediisopropylidene)-bisphenol and 4,4′di-potassium sulfonyldiphenol, the oligomer chains showed bimodal molecular weight distributions (Fig. 4). This peculiar behavior may be explained in terms of the initiators solubilities in the monomer and of the different reactivities of the initiation sites (see Section 4.1).

4.1. Theoretical results

The use of anionic and dianionic compounds, i.e. HO^- or lineal alkoxylates, for initiating the propylene oxide (PO) polymerization has been studied recently [12]. It was observed in that study that the *anti*-addition (orientation regarding to methyl group of PO) is preferred over the *syn* addition.

Regarding to the calculus of the polymerization process, the reaction mechanism will be described briefly. Two different patterns of growing are considered: (a) an unsymmetrical growing (UG), which was considered only for one side of the molecule and (b) a symmetrical growing (SG) (Fig. 5). The addition from 1 to 10 PO units was considered. For each addition of a PO unit, the energy was calculated; thus in order to obtain the energy value, the structures of the chains was first optimized at MM+ level, following optimization at AM1 level. One important point to note is that only an *anti*-addition was considered regarding the above calculation. Another point is that only the less substituted carbon atom of the epoxide molecule undergoes the attack of the nucleophile species as in a SN_2 reaction.

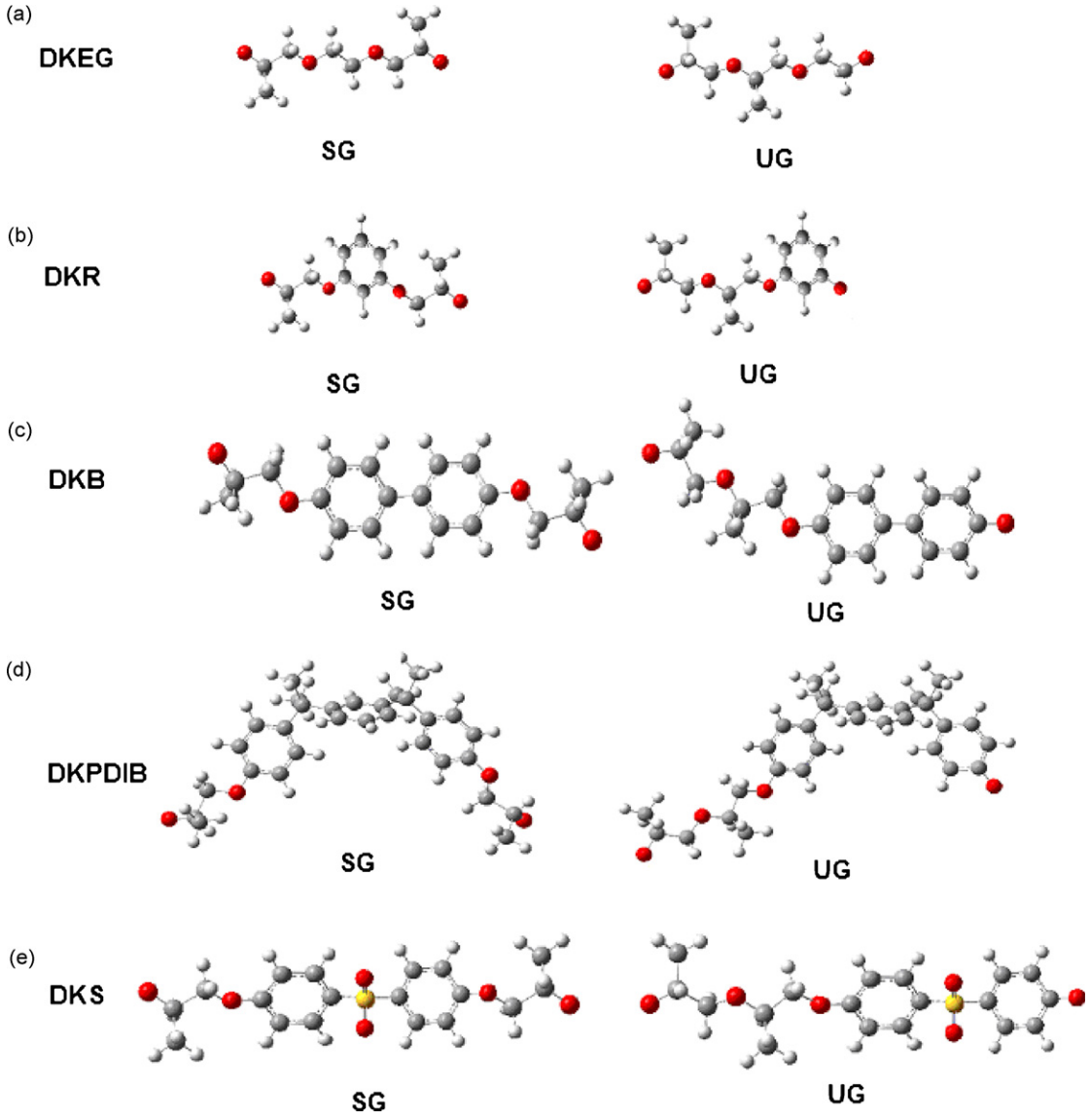

Fig. 5. Symmetrical (SG) and unsymmetrical (UG) growing of PPO chains during the AROP started with: (a) DKEG, (b) DKR, (c) DKB, (d) DKPDIB and (e) DKS initiators.

Table 3
Energy values for PO polymerization initiated by DKEG, DKR, DKB, DKPDIB and DKS

PO units	Energy (kcal/mol)		
	Unsymmetrical growing Eu	Symmetrical growing Es	Eu–Es
DKEG			
2	−54607.8	−54609.1	1.28
6	−123052.7	−123053.0	0.30
10	−191479.8	−191480.1	0.30
DKR			
2	−70057.6	−70029.5	−28.1
6	−142713.7	−142680.2	−33.5
10	−215353.8	−215319.0	−34.8
DKB			
2	−89051.1	−89023.9	−27.1
6	−161704.1	−161666.9	−37.2
10	−234347.8	−234309.0	−38.8
DKPDIB			
2	−129499.2	−129475.7	−23.5
6	−202212.4	−202178.8	−33.6
10	−274854.0	−274821.1	−32.9
DKS			
2	−108297.3	−108266.3	−31.0
6	−180927.1	−180901.3	−33.4
10	−253571.7	−253540.4	−31.3

The energy values for the polymerizations initiated by DKEG, DKR, DKB, DKPDIB and DKS are listed in Table 3. The purpose of obtaining the Eu–Es value is to define the preference of the growing; thus, a positive Eu–Es value means a preference for a symmetrical growing, whereas for a negative value, unsymmetrical growing is preferred. Regarding to the aliphatic glycolates, the Eu–Es values are ranging between 0.30 and 1.28 kcal/mol, which implies a little preference for a symmetrical growing (see DKEG values in Table 3). It must be expected for such kind of regular propagation the formation of a monodisperse population of polymer chains.

In contrast, for the aromatic initiators the Eu–Es value, ranging between −28.1 and −46.5 kcal/mol (see Table 3), shows a higher preference for an unsymmetrical over a symmetrical growing. This energetic difference could be due to resonance effects in the aromatic fragment, which are more intensive during an unsymmetrical growing because of the presence of an oxygen atom with negative charge. This negative charge is delocalized over the aromatic ring, obtaining a system with lower energy. Therefore, it can be established that the introduction of the aromatic segment from the initiator molecule affects considerably the growing patterns of the polymer chains. The unsymmetrical growing observed by quantum calculations implies that polymers chains with different lengths and high polydispersity are obtained.

On the other hand, the DKS system posses a sulfoxide fragment, which is an electron-attracting group. However, the presence of this fragment did not have an important effect on the Eu–Es gap value. Therefore, it is possible to affirm that the electron-donating groups, like oxygen atoms or alkyl group in the DKPDIB system, have more weight in the energy value.

5. Conclusions

Propylene oxide oligomers were synthesized by AROP using a range of different di-potassium glycolates. A glycolate with a linear structure (di-potassium ethylene glycolate) and a set of aromatic glycolates (di-potassium resorcinolate, 4,4′-bisphenolate A, 4,4′-(1,3 phenylenediisopropylidene)-Bisphenolate and 4,4′-sulfonyldiphenolate) were compared as initiators of the PO polymerization. The employment of a lineal glycolate (DKEG) produced very monodisperse PPO, as the characterization by SEC revealed. Oligomers with a lower monodispersity were synthesized when the di-potassium resorcinol salt initiated the polymerization. On the other hand, very polydisperse oligomers, even with a bimodal molecular weight distribution, were obtained when the polymerizations were started by other less soluble aromatic initiators. Indeed, there is a correlation between the polymer polydispersity and the initiator solubility, which depends on the number of aromatic rings in the structure. This influence of the aromatic structure on the molecular weight distribution was clarified by theoretical methods. Indeed, the quantum semiempirical calculations revealed for these aromatic systems that various propagation patterns are possible, due to the very different Eu–Es energy values associated to the unsymmetrical propagation from the two reactive sites in the aromatic glycolates. The irregular growing of polymer chains initiated by aromatic compounds may be correlated to high polydispersities detected by SEC.

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