

Ionic liquids as modifier for the oligomerization of α -olefins to reactive poly(α -olefins) via traditional AlCl_3 catalyst

Miad Mashayekhi^a, Leila Moballegh^{a,*}, Naeimeh Bahri-Laleh^a, Samahe Sadjadi^a, Albert Poater^{b,*}

^a Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14975/112, Tehran, Iran

^b Departament de Química, Institut de Química Computacional i Catàlisi, Universitat de Girona, c/ M^o Aurèlia Capmany 69, Girona, Catalonia 17003, Spain

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ABSTRACT

In the polymerization there are series of systems that are traditionally used because their procedures are well established, and it is not considered necessary to leave the comfort zone. Here, it is proposed to reevaluate the cationic initiator system with a trident of IL/ $\text{AlCl}_3/\text{H}_2\text{O}$ (IL: ionic liquid). Thus, different ILs comprising of similar anionic part, however various cationic moieties; based on triethanolamine (TEA), tributylamine (TBA), and pyridine (Pyr) precursors; were synthesized and evaluated together with AlCl_3 in the cationic polymerization of 1-decene. According to the GPC results, while Pyr and TBA-based ILs suppressed molar mass of poly(α -olefins) (PAO), compared to PAO from neat AlCl_3 , TEA containing IL enhanced it. This affirms outstandingly higher performance of the IL/ AlCl_3 than $\text{AlCl}_3/\text{H}_2\text{O}$. According to the ^{13}C NMR data, PAOs from IL containing initiators have higher content of long chain branching, which is beneficial to improved viscosity index characteristic. Kinematic viscosity results were in accordance with the molar mass and ^{13}C NMR data. ^1H NMR spectra point to the fact that PAOs derived from TEA and TBA-based ILs generate exo-olefins, a type of vinyl that leads to reactive oligomers with potential capacity for block copolymers. DFT theoretical calculations and studies of non-covalent interactions help to separate and understand how the nature of the IL translates into such different properties.

1. Introduction

The synthetic oils based on poly(α -olefins), PAOs, are highly efficient fluids, which are produced from the oligomerization of higher α -olefins [1–3], such as 1-hexene and 1-octene [4–6], and more specially 1-decene [7–10]. These PAO oils have an incredible variety of applications, including automotive crankcase lubrication, motor oil production, automatic gearbox oil, hydraulic oil, compressor oil, heat transfer fluids, food grade oils and etc. [11–14]. A wide range of thermal performance, oxidative stability, hydraulic and shear stability, low corrosion and toxicity and high compatibility with mineral oils render PAOs highly favorable compared to mineral oils. Moreover, PAOs benefit from high lubricating properties [15,16], higher viscosity index, lower pour point, lower toxicity and higher smoke point, making them an excellent alternative to conventional oils [17,18]. So, there is a growing demand for PAO in the industrial sector [19,20].

Various techniques have been reported for the synthesis of PAOs, including the use of coordination catalysts [21–23], Lewis-acid

co-initiator systems, such as AlCl_3 [24–27] and BF_3 [23,28] along with a protonic initiator, such as H_2O or alcohol, and also employing liquid coordination complexes [29,30] and ionic liquids (ILs) [30,31,32]. While BF_3 is commercially preferred to produce oils with low KV^{100} (kinematic viscosity at 100 °C): 2–10 cSt, AlCl_3 is usually used for producing oils with higher $\text{KV}^{100} > 10$ cSt [33]. In the recent years, there has been increasing interest in the use of ILs as green solvents and catalysts in polymerization reactions, including polymerization of α -olefins to form PAOs [34–36]. The use of ILs can provide advantages, such as improved product quality, increased reaction rates, and reduced waste compared to traditional methods. Additionally, the use of green synthesis methods can help to reduce the environmental impact of polymer production.

Ziegler Natta catalysts have also been used to produce high molecular weight oils KV^{100} : 40–100 cSt and in this line, metallocene type catalysts are used for the preparation of PAOs with precise and uniform microstructure [37–39], even though in the industry there are more important catalytic systems [40–42]. These systems mostly rely on AlCl_3

* Corresponding authors.

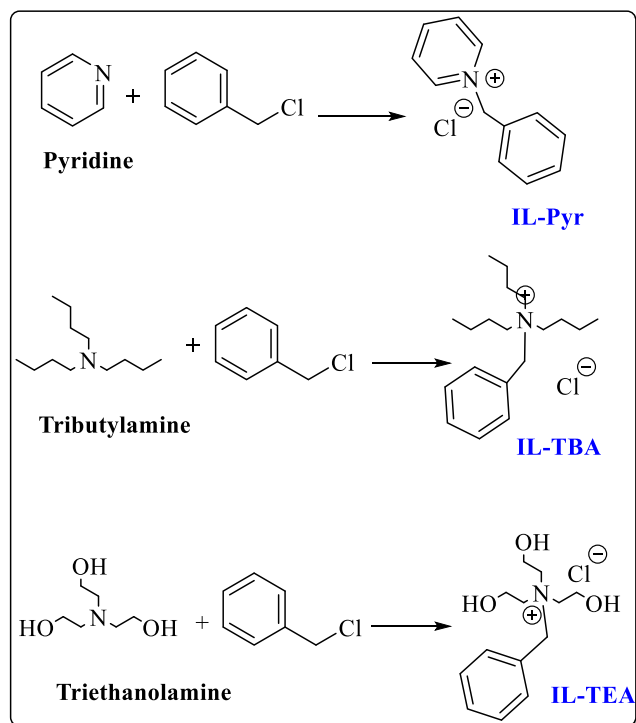
E-mail addresses: l.moballegh@ippi.ac.ir (L. Moballegh), albert.poater@udg.edu (A. Poater).

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Scheme 1. The procedure for the synthesis of ILs.

and BF_3 Lewis acidic co-initiators in complexation with alcohol based initiators [43]. Although production of PAOs in the presence of BF_3 and AlCl_3 co-initiators is industrially preferred due to their low cost and high efficiency, the corrosive nature of these catalysts motivated scientists to focus on more environmentally friendly catalysts or synthetic routes. In recent years, several reports have been reported on α -olefins oligomerization using IL catalysts as green and safe alternatives to BF_3 and AlCl_3 . In fact, ILs as organic salts benefits from various advantageous, such as facile synthesis, diversity and low-toxicity [44,45]. In this avenue, our group also tried to produce PAO using heterogeneous and homogeneous IL catalysts [32,33,46,47].

Recently, PAO using various IL/ AlCl_3 catalytic systems, in which ILs were prepared from the reaction of 1-methylimidazole with various alkyl chlorides and the effect of the nature of IL cation on the properties of the as-prepared PAO was investigated. It was found that the nature of IL could affect the properties of the synthesized PAO and among various ILs, the one prepared from the reaction of 1-methylimidazole and benzyl chloride demonstrated the highest activity toward low viscosity PAO synthesis [48,49]. Nevertheless, the PAO prepared using the mentioned initiating system had a more uniform microstructure which showed its effect on a higher VI value [46,50]. These remarkable achievements encouraged us to continue our research on this subject. Following our previous report and considering the importance of the nature of the IL cation, in this study, we investigated three different ILs (Scheme 1), derived from the reaction of benzyl chloride with pyridine,

tributylamine and triethanolamine and used them along with AlCl_3 to produce PAO. Then, the properties of the as-prepared PAOs were compared.

2. Experimental

2.1. Materials

Triethanolamine (TEA, 98%), tributylamine (TBA, 98.5%), pyridine (Pyr, 99%), NaOH (97%), benzyl chloride (99%), 1-decene (94%) and AlCl_3 (anhydrous powder sublimed, > 99%) used to either prepare the initiating systems or perform oligomerization reactions were provided from Sigma-Aldrich.

2.2. Synthesis of ILs: IL-Pyr, IL-TBA and IL-TEA

Three ILs used in this study, IL-Pyr, IL-TBA and IL-TEA, were prepared through the reaction of benzyl chloride with pyridine or aliphatic amines (TBA or TEA). In more detail, benzyl chloride (1.3 mmol) was mixed with Pyr or TBA or TEA (1 mmol) in a double-neck balloon and the mixture was stirred under N_2 atmosphere for 24 h. At the end of the reaction, the viscous liquid was collected, washed with diethyl ether and dried under reduced pressure.

2.3. Oligomerization

Oligomerization of 1-decene was performed in a stainless steel reactor equipped with circulator and gas inlets. First, the reaction vessel was purged with Ar gas at 80 °C for 1 h and then, the reactants, i.e. a mixture of AlCl_3 co-initiator and IL (0.9 g, $\text{AlCl}_3/\text{IL}=2.0$ mol/mol), and the mixture of 1-decene monomer (30 g) with deionized water ($\text{H}_2\text{O}/\text{AlCl}_3=0.5$ mol/mol) were introduced. Oligomerization was conducted at 80 °C for 50 min. Subsequently, the reaction was halted and after cooling the reactor, the as-prepared PAO was collected, and washed with NaOH solution (5 wt.%) several times. The resulting viscose oil was then heated under -0.8 bar vacuum up to 250 °C to furnish yellowish PAO oil.

It is worth to mention that, the initiator (H_2O) content not only affects the polymerization yield, but also can alter the final PAO microstructure [51,52]. Considering this fact, the polymerizations were conducted at the optimum $\text{H}_2\text{O}/\text{AlCl}_3$ amount of 0.5, reported in the previous literature [46].

2.4. Characterization

Bruker DRX400 MHz was used to record ^{13}C NMR and ^1H NMR spectra using CDCl_3 as solvent at 25 °C with 90° pulse angle, 6 s delay time, and 6000 scans for ^{13}C NMR. Kinematic viscosity was measured at 100 and 40 °C (KV^{100} and KV^{40}) based on ASTM D445 and viscosity index (VI) according to ASTM D2270. GPC Agilent 1100 was employed to determine molecular weight and the molecular weight distribution (PDI) of oils using CHCl_3 solvent with flow rate of 1.0 mL/min.

Table 1
Molecular characteristics of the synthesized PAOs using different catalytic systems¹.

Product	IL/Catalyst (mol/mol)	Yield (%)	M_n (g/mol)	M_w (g/mol)	D^2	KV^{100} (cSt)	KV^{40} (cSt)	VI
PAO- AlCl_3	0:1	78	1750	2450	1.4	32.3	246.0	132
PAO-Pyr	1:2	76	1401	1906	1.4	21.6	113.4	147
PAO-TBA	1:2	79	1400	1896	1.3	18.9	108	144
PAO-TEA	1:2	77	1955	2691	1.3	32.5	121.9	150

¹ Oligomerization conditions: Monomer= 30 g, co-initiator (AlCl_3 + IL)= 0.9 g, $T = 80$ °C, $t = 50$ min.

² Dispersity= M_w/M_n .

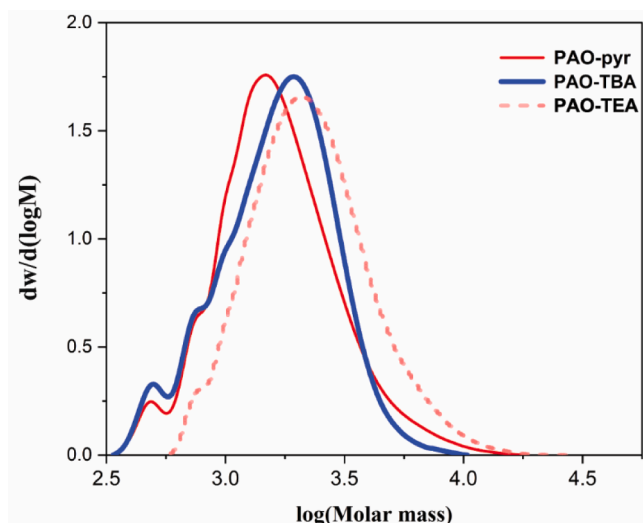


Fig. 1. Molecular weight distribution of the synthesized PAOs in the presence of different ILs.

3. Results and discussion

3.1. Molecular weight and molecular weight distribution

To study the role of cation nature of IL on the characteristics of the prepared PAO, one IL with aromatic cation, IL-Pyr, was prepared and its performance for the oligomerization of 1-decene was compared with two ILs: IL-TBA and IL-TEA, with aliphatic cations. Moreover, comparison of IL-TBA and IL-TEA can disclose the role of polarity of IL on the

features of the as-synthesized PAO.

The characteristics of PAOs synthesized using various IL/ AlCl_3 systems were compared with that of PAO from neat AlCl_3 co-initiator. As it is presented in Table 1, although the yield of the oligomerization reactions is almost similar with no significant variation, the average molecular weights are implicitly different for the PAOs prepared using different catalytic systems. More precisely, PAO-TEA showed the highest M_w of 2691 g/mol, even more than neat AlCl_3 (2450 g/mol). Moreover, M_w values of PAO-Pyr and PAO-TBA are almost similar and lower than that of PAO-TEA and AlCl_3 .

Fig. 1 shows GPC curves for the PAOs synthesized in the presence of ILs as a part of the initiating system. As shown, an obvious small peak is visible in case of PAO-Pyr and PAO-TBA. This peak has been fitted with a Schulz Flory distribution peak centered at 486.6 for both PAOs and the next visible peak can be fitted with a Schulz Flory distribution peak centered at 729.9. As the difference between the peaks molecular weights is 243.3, which is half of the 486.6, it can be deduced that the first peak is related to a dimer, while the next one is related to a trimer fraction. Considering the molecular weight of 1-decene monomer which is 140 g/mol, it should be noted that there is a difference between the real molecular weight and the one obtained from GPC result that is related to the GPC calibration which normally is done using polystyrene standards. From the above assumption it can be concluded that in the case of PAO-TEA there is no dimer fraction present.

To estimate other fractions percentage and their molecular weights, the molecular weight distributions of the PAOs were deconvoluted so that each peak represent an i -mer; $i = \text{di, tri, tetra, ...}$ Fig. 2 shows the deconvoluted molecular weight distributions. The total number of Schulz-Flory peaks used for deconvolution of the PAO-Pyr, PAO-TBA and PAO-TEA are 29, 24 and 34 peaks, respectively. For the first 19 peaks the difference of molecular weight between two peaks in a row is 243.3. However, for the rest of the peaks which belong to the higher

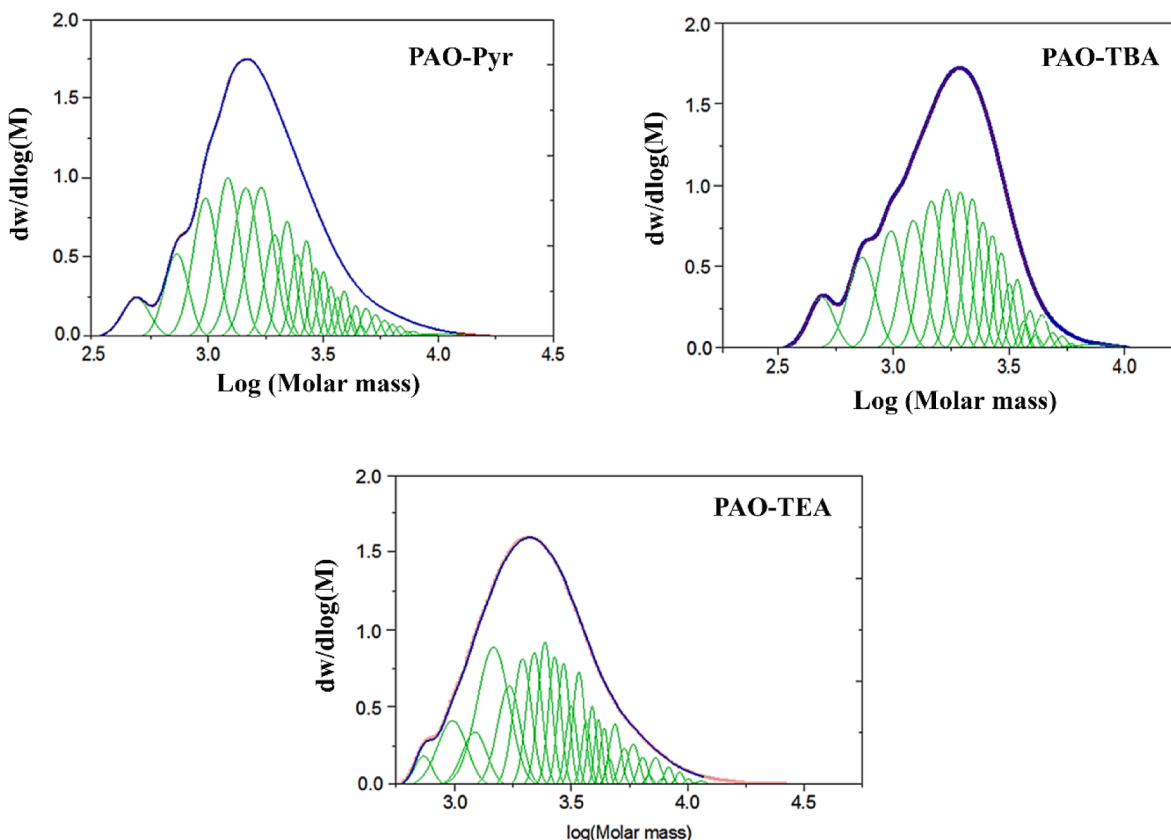


Fig. 2. Deconvoluted molecular weight distributions of oligomers to Schulz-Flory distribution peaks, representing i -mer i : di, tri, tetra,

Table 2

Peak area (%) from deconvolution of GPC graphs of the synthesized PAO samples (the first 19 peaks).

Number of monomeric units in a chain	M_w	%Peak area		
		PAO-Pyr	PAO-TBA	PAO-TEA
2	486.58	3.69	4.49	0.00
3	729.87	6.75	8.34	1.92
4	973.16	11.74	10.01	6.87
5	1216.45	13.31	9.93	4.82
6	1459.74	13.30	10.92	15.85
7	1703.03	13.03	10.87	8.18
8	1946.32	6.59	9.68	8.22
9	2189.61	6.42	8.37	7.31
10	2432.9	3.73	6.30	7.17
11	2676.19	4.24	5.20	5.69
12	2919.48	2.68	4.13	5.05
13	3162.77	2.43	2.59	3.14
14	3406.06	1.73	2.83	4.85
15	3649.35	1.28	0.93	2.07
16	3892.64	1.56	1.27	2.42
17	4135.93	0.60	0.43	1.82
18	4379.22	0.92	1.48	1.61
19	4622.51	0.29	0.58	0.77
20	4865.8	1.07	0.47	2.55

molecular weights with lower fractions the difference between two peaks in a row is higher to avoid sophistication and reducing the number of peaks. Table 2 shows the first 19 peaks characterization.

3.2. Kinematic viscosities and viscosity index

Kinematic viscosities at 100 and 40 °C are presented in Table 1. The relatively higher kinematic viscosity of PAO-TEA, at 100 °C, than that of PAO-Pyr and PAO-TBA, is observable which is in accordance with higher molecular weight of PAO-TEA. However, the KV⁴⁰ results show that there is a huge difference between the PAOs synthesized with traditional AlCl₃/H₂O catalyst and the PAOs synthesized using ILs. So that the kinetic viscosity of PAOs at 40 °C obtained in the presence of the as-synthesized ILs is relatively half of neat AlCl₃. Considering the relatively close molecular weights of the oils produced using IL/AlCl₃ and AlCl₃ catalysts, it can be concluded that the chain branching should be considerably lower in the case of IL/AlCl₃ based PAOs that shows induced coordination in oligomerization of 1-decene in the presence of ILs.

The high value of VI related to the PAOs synthesized using IL/AlCl₃ suggests better performance of the oligomers and another clue for lower chain branching of the oligomers synthesized in the presence of ILs in comparison with the oligomer synthesized using neat AlCl₃. Among three oligomers synthesized by ILs, the highest VI belongs to the PAO-TEA. It is suggested that the higher average molecular weight of the PAO-TEA is responsible for the higher VI which is in accordance with the literature [53,54].

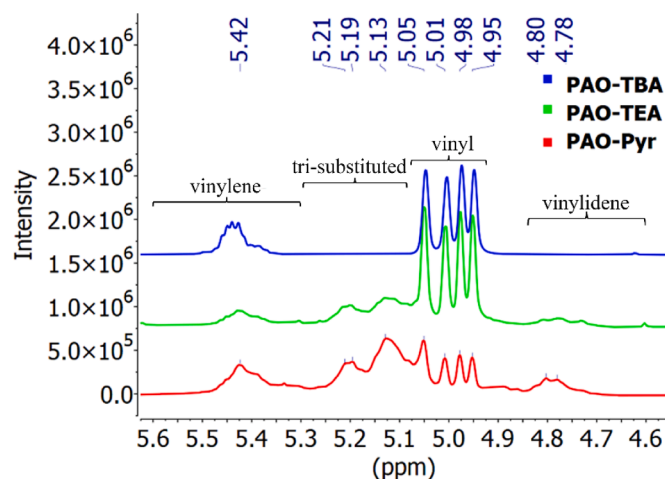


Fig. 3. ¹H NMR spectra of synthesized PAOs via different catalyst systems in the vinyl region.

Table 3

The unsaturation types resulted by different termination mechanisms.

	Vd	3Vn	2Vn	Vn
PAO-AlCl ₃	11.2	0.63	25.4	0.00
PAO-Pyr	0.08	0.46	0.21	0.25
PAO-TBA	0.003	0.00	0.25	0.74
PAO-TEA	0.01	0.27	0.08	0.64

3.3. NMR analysis

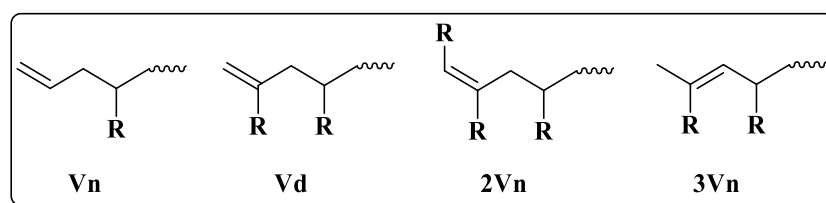
For studying the microstructure of oligomers and the influence of the cation in IL [55], ¹³C NMR and ¹H NMR spectra of the samples were investigated.

3.3.1. End unsaturation of the synthesized PAOs

The type of C = C unsaturation in PAO chains was investigated using ¹H NMR spectra. Scheme 2 shows the various possible unsaturation types.

Fig. 3 shows ¹H NMR spectra in the vinyl region where three peaks of vinylene (2Vn), tri-substituted vinylene (3Vn), vinylidene (Vd) and vinyl (Vn) are usually appeared, where chemical shifts of 4.6–4.85 ppm, 4.9–5.12 ppm, 5.12–5.30 ppm and 5.3–5.62 ppm are related to Vd, Vn, 3Vn and 2Vn, respectively [56].

Table 3 shows the area under peaks and calculated percentage of each unsaturation type bond. The table shows that in the case of PAO-Pyr and AlCl₃/H₂O, the most dominant unsaturation type is tri-substituted which is related to 1,2 insertion mechanism and β-hydride transfer after isomerization or rearrangement [57]. It is interesting that in the case of PAO-TBA, the dominant type of termination (73.5%) is vinyl type and it is resulted as termination by the mechanism of β-alkyl transfer [56]. Besides, it is exciting that in the case of PAO-TBA tri-substituted vinylene has not occurred and vinylidene type of unsaturation is negligible. Also, in the case of PAO-TEA, the same as



Scheme 2. Molecular structure of possible unsaturated C=C bonds in the structure of crude PAO chains.

Table 4
Branching characterization of PAOs based on ^{13}C NMR analysis.

	Surface area under peaks at 11–17ppm	Surface area under peaks at 18–44 ppm	main CH_3 peak (ppm 14.1)	Sum of all other CH_3 peaks	Branching ratio	% short chain branching
PAO-Pyr	1.42	15.37	1	0.42	0.090	29.5%
PAO-TBA	1.22	10.16	1	0.22	0.114	18.0%
PAO-TEA	1.38	14.14	1	0.38	0.095	27.5%
PAO- AlCl_3	1.43	15.84	1	0.43	0.090	30.0%

Table 5
Distribution of the Short-chain branches based on ^{13}C NMR analysis.

	PAO-Pyr	PAO-TBA	PAO-TEA	PAO- AlCl_3
Short-chain methyl (19.7)	0.19	0.07	0.16	0.20
Short chain ethyl (10.92)	0.04	0.02	0.05	0.03
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2$ (22.6)	0.03	0.05	0.04	0.02
$\text{CHCH}_2\text{CH}_2\text{CH}_3$ (14.5)	0.07	0.04	0.04	0.10
$\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ (14.3)	0.06	0.04	0.06	0.06
Others	0.03	0.00	0.03	0.02
Sum of all short-chain branches	0.42	0.22	0.38	0.43

$$\text{Br} = \frac{[15 \times \sum(^{13}\text{C} \text{ integral } 11-17 \text{ ppm})]}{[15 \times \sum(^{13}\text{C} \text{ integral } 11-17 \text{ ppm}) + 14 \times \sum(^{13}\text{C} \text{ integral } 18-44 \text{ ppm})]} \quad (1)$$

PAO-TBA, the dominant termination type is β -alkyl elimination. So, it is concluded that PAO-TBA and PAO-TEA are highly reactive oligomers.

3.3.2. Branching type and content

The branching content (br) and the percentage of short chain branching (%) is usually calculated using the following equations [58]:

$$\text{Short-Chain branching} = \frac{\sum(^{13}\text{C} \text{ integral short-chain methyl})}{\sum(^{13}\text{C} \text{ integral all methyl } 11-17 \text{ ppm})} \times 100 \quad (2)$$

Table 4 shows the branching content and short chain branching percentage. As can be seen the branching content and the percentage of short chain branching are significantly lower in the case of PAOs based on IL/ AlCl_3 which is in accordance with the high VI of the samples.

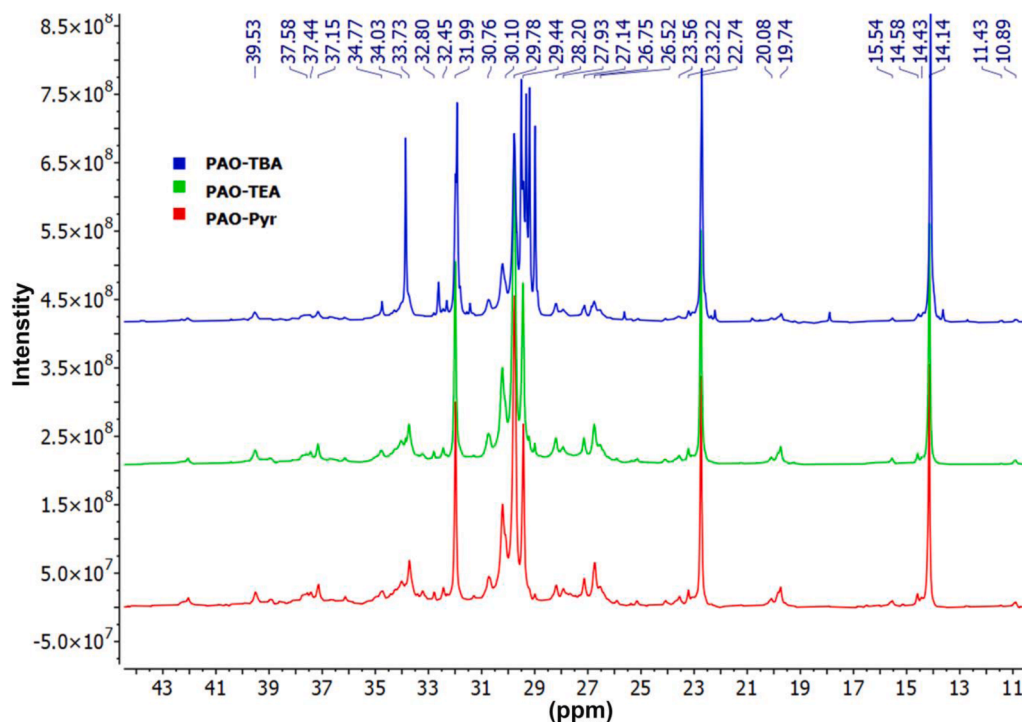


Fig. 4. ^{13}C NMR spectra of synthesized PAOs assisted by different IL systems.

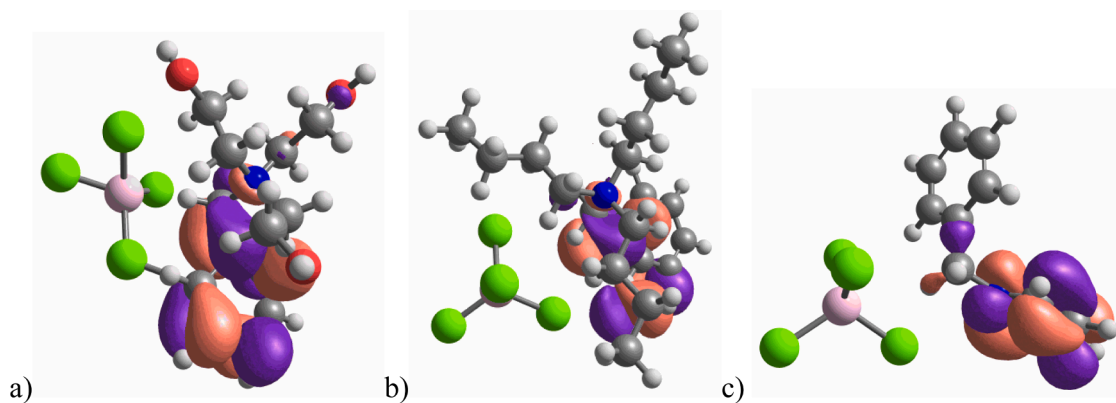


Fig. 5. LUMO plots for complexes: (a) PAO-TEA, (b) PAO-TBA, and (c) PAO-Pyr.

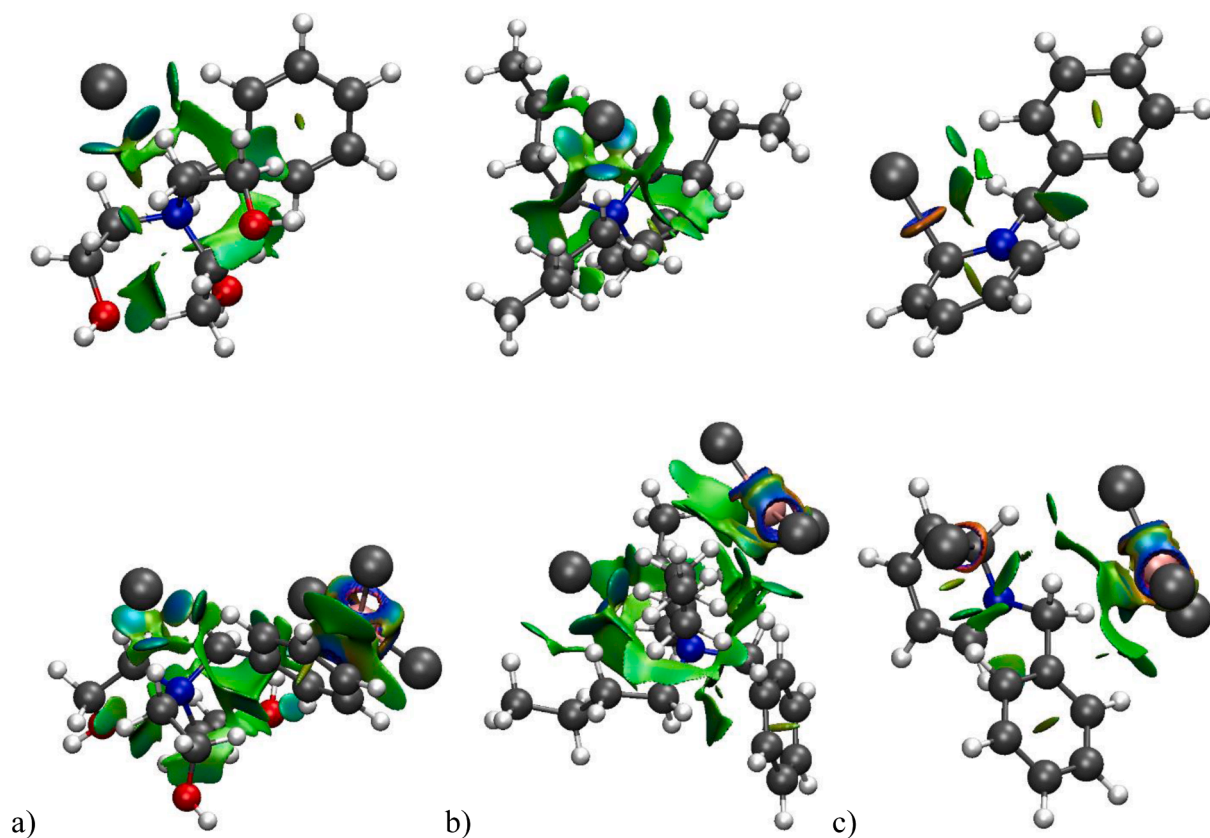


Fig. 6. Isosurface NCI plots for complexes: (a) PAO-TEA, (b) PAO-TBA, and (c) PAO-Pyr (obtained for a value of 0.5 on the reduced density gradient. For the color scale, we used blue (attractive) and red (repulsive); the big balls in gray are chlorides, above/below without/with AlCl_3).

Comparing PAOs, synthesized using ILs, it can be seen that the branching content of PAO-Pyr and PAO-TEA is lower than PAO-TBA and this fact explain the relatively higher VI of PAO-TEA and PAO-Pyr than that of PAO-TBA.

Table 5 shows the relative distribution of short chain branching types and it demonstrates that the short chain methyl is the dominant short chain branch type in all PAOs (Fig. 4).

3.4. Computational studies

Due to the ionic character presented by the interaction between both charged parts of the ILs tested, we envisaged Density Functional Theory (DFT) calculations first to unveil the binding energy of the chloride with

the positive moiety. Thermodynamically, there is a natural evolution leading to a binding energy of chloride in the cationic unit of 26.4, 28.9 and 32.6 kcal/mol for PAO-TBA, PAO-Pyr and PAO-TEA, respectively (see Table S1). Then taking as a reference that AlCl_3 adopts a chloride anion with a relative stabilization of 50.3 (an isolated chloride anion is taken into account as a reference), values of 41.7, 53.6 and 54.9 kcal/mol are obtained for PAO-TEA, PAO-TBA and PAO-Pyr, respectively. But it is necessary to reread these values, they are already obtained from the species where AlCl_3 has been incorporated into the corresponding IL. This implies an entropic destabilization, which is much smaller for PAO-TEA, 20.0 kcal/mol, than PAO-TBA and PAO-Pyr with 32.4 and 34.2 kcal/mol, and which is corrected with the subsequent interaction of AlCl_3 with the anion chloride. Thus, it is necessary to read the final

stabilization value of 19.4, 21.7 and 22.5 kcal/mol, for PAO-TBA, PAO-TEA and PAO-Pyr. These are results that reveal a potential line of reactivity. Electronically, going to the analysis of the Natural Population Analysis (NPA) charges in Table S2, we can only highlight the more negative charge on the chlorine of the IL of the systems with PAO-TEA (−0.739) and PAO-TBA (−0.740) with respect to PAO-Pyr (−0.463). However, an analysis with conceptual DFT becomes key, which leads to see that the chemical hardness, in Table S2, once AlCl₃ is incorporated in the simulations, is much lower for PAO-Pyr (0.080) compared to PAO-TBA (0.137) and PAO-TEA (−0.152), which present quite similar values. This also results in the fact that the Parr electrophilicity [59] of the latter systems is ostensibly lower, 0.084 and 0.080 compared to 0.207 for PAO-Pyr [60]. In detail, the difference is with the lowest unoccupied molecular orbital (LUMO), which in the case of the PAO-TBA and PAO-TEA suffers a substantial destabilization with respect to the one corresponding to the PAO-Pyr, of 0.059 and 0.062 a.u., respectively (see Fig. 5). Particularly, the CH₂ moiety does not participate in the LUMO for PAO-Pyr, whereas is conjugated in the π system for the others. Actually, the pyridine ring is able to lead to this stabilization, while the other two systems, omitting it and instead owing alkyl chains, play with a phenyl ring.

This above computational study was followed by the study of the non-covalent interactions (NCIs), computed with the NCI plots in Fig. 5 using the NCIPLOT package of Contreras-Garcia et al. [61,62].

The NCI plots in Fig. 6 allow to observe and qualitatively evaluate the strength of the non-covalent interactions between the two charged moieties [63,64]. In the representations, we plotted the isocontour [65]. PAO-TEA includes 4 favorable interactions with Cl...H hydrogen bonds. And then you do not have to forget other H-bonds also very strong O...H, in fact 6, since there are 3 oxygen atoms and each generates 2 H-bonds. PAO-TBA has only 3 strong direct Cl...H interactions, but it is necessary to add 2 more at greater distance. However, in the rest of the molecule there are no relevant non-covalent interactions except for some H...C_{aryl}, coming from the π system of the aryl. The simplified PAO-Pyr system is of a different nature since, although it has only two Cl...H-bonds, it has a C—Cl covalent/ionic type bond with the aromatic ring. This is demonstrated by a relatively higher bond index of 0.597 [10,66–68], using the Mayer Bond Order (MBO) approach [69]. With the addition of AlCl₃, the strongest H-bonds are observed for the PAO-TEA system thanks to the favorable interactions of the hydroxyls and the entering AlCl₃.

4. Conclusions

In this work the performance of three ILs containing initiator systems and traditional neat AlCl₃/H₂O system were investigated. The results showed that despite nearly close molecular weights, the kinematic viscosities of PAOs obtained from IL-based systems, at low temperature, were considerably lower than the traditional AlCl₃/H₂O catalyst and at the same time the VI of the IL-derived PAOs is obviously higher than that of the traditional catalyst with the highest amount in the case of PAO-TEA. This implies significantly higher performance of the IL/AlCl₃ than AlCl₃/H₂O. The GPC results showed that the molecular weight of the PAO-TEA is slightly higher than the other PAOs. From GPC deconvolution it was deduced that the three highest molecular weight fractions belong to pentamer, hexamer and heptamer fractions in the case of PAO-Pyr and PAO-TBA, and hexamer, heptamer and octamer fractions in the case of PAO-TEA. The ¹³C NMR analysis confirmed lower branching ratio and short chain branching of PAOs based on ILs than the traditional AlCl₃/H₂O. Also, ¹H NMR showed that the dominant type of unsaturation in the case of PAO-TEA and PAO-TBA is vinyl type which is reactive and as a result the mentioned oligomers can be classified as reactive oligomers and can have potentially important applications like synthesis of block copolymers. In addition, the computational study of non-covalent interactions made it possible to establish a trend between the systems studied, with a prevalence for the PAO-TEA system, with more accumulation of H-bonds.

CRedit authorship contribution statement

Miad Mashayekhi: Investigation, Writing – original draft. **Leila Moballegh:** Investigation, Writing – original draft, Conceptualization, Writing – review & editing. **Naeimeh Bahri-Laleh:** Visualization, Conceptualization, Writing – original draft, Writing – review & editing. **Samah Sadjadi:** Conceptualization, Writing – review & editing. **Albert Poater:** Investigation, Visualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

There are no conflicts of interest

Data availability

A summary is collected in the supporting information file and then more details are available upon request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2023.113403.

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