

Oligomerization of olefins in a chloroaluminate ionic liquid

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Abstract

Linear 1-olefins are oligomerized to dimers, trimers and tetramers by the Lewis acidic (excess of 0.1 mol equivalent AlCl_3) ionic liquid [1-butyl-3-methylimidazolium][tetrachloroaluminate], even in the presence of ethylaluminiumdichloride. Addition of titaniumtetrachloride, however, generates branched, atactic polymers with narrow monomodal polydispersities as waxy or oily compounds in high yields. Molar masses vary from $M_w = 650$ to 1620 g/mol ($M_n = 440$ – 970 g/mol) independent of the monomer used. Predominantly 1,1,2-trisubstituted double bonds are formed by a migration mechanism in the termination step of the oligomerization process. In contrast, polymerization of ethene by titaniumtetrachloride in the conventional solvent toluene, affords mainly linear polyethene with a broader polydispersity and a higher molar mass.

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1. Introduction

Within the last 15 years ionic liquids have experienced a renaissance, especially since these liquids, consisting of ion pairs, find applications as solvents in biphasic catalysis. While the first ionic liquid was already synthesized in 1914 [1,2], it was only once the first reports of their use as reaction media for organic syntheses appeared that their importance became apparent to the broader scientific community [3]. Ionic liquids show an unique combination of properties including high polarity, low viscosity, high liquid temperature range, high thermal

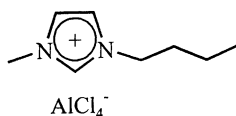
stability, wide tunability, immiscibility with certain organic solvents and no effective vapour pressure [4–7]. Typical components are 1-alkylpyridinium, 1,3-dialkylimidazolium, ammonium or phosphonium cations and halide, AlCl_4^- , PF_6^- , SbF_6^- , BF_4^- or BPh_4^- anions. Ionic liquids have been utilized in, for example Friedel-Crafts [3,8,9], aromatic substitution [10], acylative cleavage [11] and Heck reactions [12,13], as well as in hydroesterification [14], carbonylation [15], hydrogenation [16–18], hydroformylation [19–23], dimerization [24–27], and polymerization [28,29] affording often novel or unusual chemical reactivities.

In this paper, the reactivity of the Lewis acidic (excess of 0.1 mol equivalent AlCl_3) ionic liquid [1-butyl-3-methylimidazolium][tetrachloroaluminate] (Scheme 1) in the presence of ethylaluminiumdichloride toward the oligomerization of 1-olefins is reported. Furthermore, the use of this liquid as a solvent

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Scheme 1.

for the biphasic oligomerization of 1-olefins by titaniumtetrachloride is described.

2. Experimental

All reactions and manipulations were carried out under a dry argon atmosphere using standard Schlenk [30], vacuum-line and glovebox techniques. All solvents were dried and purified by conventional methods and were distilled under argon prior to use. Melting points were measured by differential scanning calorimetry (second run) on a Du Pont 2100 apparatus at a heating/cooling rate of 10 °C/min. NMR spectra were recorded on a Varian VXR 300 spectrometer (^1H , 300 MHz at 25 °C; $^{13}\text{C}\{^1\text{H}\}$, 75.48 MHz at 100 °C). Chemical shifts are reported in ppm relative to the ^1H and ^{13}C residue of the deuterated solvents. Gel permeation chromatographic analyses were performed at a flow rate of 1.0 ml/min in THF at 30 °C using a Waters modular system (detector RI 410; polymers obtained in the ionic liquid) or at 100 °C using a Waters 515 autosampler thermo separation product AS 100 (detector RI 410; polymer obtained in toluene) with reference to a polystyrene calibration curve. Gas chromatographic separations were carried out on a Perkin-Elmer autosystem XL with a 15 m \times 0.32 mm fused silica column. Depending on the used substrates the internal standards butane, pentane, hexane, heptane, octane, nonane, decane and/or dodecane (Aldrich) were used. 1-Butyl-3-methylimidazolium chloride was prepared according to a published procedure [31]. [1-Butyl-3-methylimidazolium][tetrachloroaluminate]/0.1 mol equivalent AlCl_3 was prepared by slowly adding 1.1 mol equivalent aluminium(III)chloride (Aldrich, sublimed twice before use) to 1.0 mol equivalent of 1-butyl-3-methylimidazolium chloride over a period of 8 h [32]. Ethylaluminiumdichloride was obtained by removing the solvent of a 10% solution in toluene (Aldrich) under vacuum (10^{-5} bar). Ethene,

propene (Afrox), 1-butene and titaniumtetrachloride (Aldrich) were used as purchased. 1-Pentene, 1-hexene (SASOL) and 1-octene (Aldrich) were dried by distillation from lithiumaluminiumhydride prior to use.

2.1. General procedure for oligomerization experiments

Typically the slightly yellow ionic liquid [1-butyl-3-methylimidazolium][AlCl_4]/0.1 mol equivalent AlCl_3 (25 mmol), ethylaluminiumdichloride (2.5 mmol), titaniumtetrachloride (9 mmol), and a magnetic stirring bar were placed in a glass lined 300 ml stainless steel autoclave. The vessel was placed in a thermostatically controlled oil bath at the given temperatures and charged with ethene, propene or 1-butene (250 mmol) at the stated pressures. After the desired reaction time, the stirred apparatus was cooled to 0 °C and opened. Any colorless organic layer formed was decanted off and immediately analyzed by GC. The remaining content was worked up by carefully adding methanol (20 ml) containing HCl (5 ml, 35% in water) and stirring for 10 h at room temperature. Any newly formed colorless organic fraction was decanted off, washed five times with methanol (15 ml) and dried under a vacuum (10^{-5} bar). The experiments with 1-pentene, 1-hexene and 1-octene (100 mmol) were carried out analogously in a high pressure Schlenk tube with PTFE sealing. The reported results represent the average of two experiments, which did not differ by more than 3%.

3. Results and discussion

Extensive experiments with the Lewis acidic (excess of 0.1 mol equivalent AlCl_3) ionic liquid [1-butyl-3-methylimidazolium][tetrachloroaluminate] (Scheme 1) were performed in the presence of 1-olefins in order to use this system in future as a solvent for polymerizations catalyzed by neutral and cationic bis(cyclopentadienyl)lanthanoid complexes. The excess of AlCl_3 leads to the formation of typical anionic species like Al_2Cl_7^- and $\text{Al}_3\text{Cl}_{10}^-$ [7] but to simplify matters, AlCl_4^- is used throughout this text. The excess of AlCl_3 was chosen, since neutral or Lewis basic ionic liquids are less suitable for

Table 1

Isolated yield (by weight) and product distribution (by GC) of [1-butyl-3-methylimidazolium][AlCl₄⁻]/0.1 mol equivalent AlCl₃/0.1 mol equivalent EtAlCl₂ oligomerized 1-olefins at 60 °C after 16 h

Monomer	Overall yield (%)	Dimers (%)	Trimers (%)	Tetramers (%)
Ethene ^a	67	25	36	6
Propene ^b	59	52	5	2
1-Butene ^c	31	30	1	0
1-Pentene ^c	12	11	1	0
1-Hexene ^c	7	6	1	0
1-Octene ^c	4	3	1	0

^a 55 bar.

^b 7 bar.

^c 1 bar.

polymerization reactions [5,27]. Furthermore, 0.1 mol equivalent of the scavenger ethylaluminiumdichloride was added to eliminate even traces of moisture in the ionic liquid by forming ethane and, thus preventing cationic side reactions by super acidic protons [3,24,27,32].

Surprisingly significant reactivity of the modified ionic liquid toward the oligomerization of ethene was observed [33]. Oligomerization and polymerization brought about by ionic liquids on their own is known, but it should not occur in the presence of scavenger ethylaluminiumdichloride [34,35]. In such a situation, nickel catalysts are generally required for oligomerization [25,36–38] and titanium catalysts for polymerization (1-olefins; chloroaluminate ionic liquids) [28,39]. In the experiments we report here, however, ethene was converted to dimers, trimers and tetramers in 67% yield within 16 h without further addition of a transition metal compound. The products were possibly not detected previously due to their slow formation and their volatility. Another reason might be that the solvent system is very sensitive to its relative composition (AlCl₃ excesses of 0.1–0.22 mol equivalent were used in the previous experiments [6,25,34,35,37,38]).

Even the higher 1-olefins propene, 1-butene, 1-pentene, 1-hexene and 1-octene were now converted into corresponding oligomers in 4–59% yield (Table 1). As expected, the formation of higher oligomers became unfavourable and the total yield of oligomers decreased with increasing chain length of the monomer (note that some of the reaction pressures vary due to the inherently related different vapour

Table 2

Isolated yields (by weight) and properties of [1-butyl-3-methylimidazolium][AlCl₄⁻]/0.1 mol equivalent AlCl₃/0.1 mol equivalent EtAlCl₂ oligomerized 1-olefins in the presence of TiCl₄ at 60 °C after 4 h

Monomer	Yield (%)	<i>M_w</i> (g/mol)	<i>M_n</i> (g/mol)	<i>D</i>	<i>T_m</i> (°C)	<i>n^a</i>
Ethene ^{b,c}	56	1620	970	1.7	116	35
Ethene ^b	58	1290	530	2.5	115	19
Propene ^{c,d}	63	740	490	1.5	–	12
Propene ^d	70	650	440	1.5	–	10
1-Butene ^e	61	1340	850	1.6	–	15
1-Pentene ^e	98	1190	770	1.5	–	11
1-Hexene ^e	81	1110	750	1.5	–	9
1-Octene ^e	72	1270	890	1.4	–	8

^a Number of monomer units in the product.

^b 55 bar.

^c 30 °C.

^d 7 bar.

^e 19 h, 1 bar.

pressures of the substrates). After the reactions no visible degradation of the reaction media was detected. Due to the hydrolytic work up procedure, no recyclization of the reaction medium was attempted. At the end of the reaction, the oligomers were readily separated from the ionic liquid by decantation. The products were analyzed by high temperature ¹³C{¹H} NMR measurements in a 10/1 (v/v) mixture of 1,2,4-trichlorobenzene/C₆D₆ and by gas chromatographic separation. The complexity of the spectra and gas chromatograms indicated a fairly unselective reaction mechanism and various isomers were formed. A complete assignment of all the signals and peaks was not possible and the formation of chlorine containing products by Lewis acid catalyzed side reactions can not be excluded.

In the presence of titaniumtetrachloride, however, waxy oligomers from ethene or oily oligomers from the higher 1-olefins propene, 1-butene, 1-pentene, 1-hexene or 1-octene were formed in up to 98% total yield (Table 2). These yields were much higher than those obtained in the absence of titaniumtetrachloride. Again the products were easily decanted from the reaction mixture. Depending on the reaction temperature, molar masses of *M_w* = 1290–1620 g/mol and *M_n* = 530–970 g/mol were determined by GPC for polyethene and molar masses of *M_w* = 650–1340 g/mol as well as *M_n* = 440–890 g/mol for the polymers of the higher 1-olefins. Oligomers with

similar molar masses were obtained independent of the monomer used. Either chain termination reactions became dominant due to slow movement of the hydrocarbon chain on the metal [40], or the growing unpolar hydrocarbon chain started to float on the reaction medium whenever a certain chain length was reached so that no further coordination to the active catalyst in the ionic liquid could occur. The slower rate of chain termination and better solubility of the substrates in the ionic liquid at lower temperatures explain the higher molar masses of the polyethene and polypropene samples formed at 30 °C. Furthermore, the oligomerizations were unexpectedly selective and gave narrow, monomodal polydispersities of $D = 1.4$ – 2.5 . Since an already narrow polydispersity of two is predicted by Schulz–Flory statistics for polymers arising from identical centers with a fixed rate of chain propagation and termination [41], the low polydispersities must be attributed to the decreasing solubility of the product in the ionic liquid with increasing degree of oligomerization and the fact that oligomers with low molar masses were washed out during the work up. Some representative analytical results of the oligomeric products are summarized in Table 2.

The polyethene samples melt at $T_m = 116$ and 115 °C (linear polyethene with higher molar mass: $T_m = 141.4$ °C) [42] while the other oligomers are

already liquid at room temperature. High temperature $^{13}\text{C}\{^1\text{H}\}$ NMR were carried out for all produced oligomers. For the oligomers of ethene and propene a branched and atactic (propene only) substitution pattern was determined by comparison to previously published assignments [43]. The spectra of the other oligomers are very complicated and the literature data are also too limited to proof a branched and atactic substitution pattern. In addition, all polymers were analyzed by ^1H NMR spectroscopy at 25 °C in CDCl_3 in order to obtain information about the chain growth and chain termination mechanisms. Four different groups of signals were observed and attributed to vinylidene, vinyl, 1,1,2-trisubstituted and vinylene end groups (Table 3) [44–46]. A vinylidene end group can be formed after 1,2-insertion of the monomer into the growing polymer chain and β -hydride elimination. The vinylene end groups are formed in a similar way after 2,1-misinsertion followed by β -hydride elimination. It is striking that the amount of product containing the thermodynamically most stable 1,1,2-trisubstituted double bond is significantly higher compared to reactions in the conventional solvent toluene [47]. This can be attributed to the fact that after the 1,2-insertion or 2,1-misinsertion, the necessary cationic intermediate for the migration of the metal moiety along the carbon backbone before β -hydride elimination, is better

Table 3

End group analyses (%) of the oligomers obtained in [1-butyl-3-methylimidazolium][AlCl_4^-]/0.1 mol equivalent AlCl_3 /0.1 mol equivalent EtAlCl_2 by ^1H NMR (300 MHz at 25 °C in CDCl_3)

Monomer	Vinylidene $\text{RR}'\text{C}=\text{CH}_2$ (4.70–4.76 ppm)	Vinyl $\text{RHC}=\text{CH}_2$ (4.90–5.15 ppm)	1,1,2-Trisubstituted $\text{RR}'\text{C}=\text{CHR}''$ (5.15–5.25 ppm)	Vinylene $\text{RCH}=\text{CHR}'$ (5.30–5.60 ppm)
Ethene ^a	21	3	60	16
Ethene ^b	10	2	11	77
Propene ^a	16	0	79	5
Propene ^b	5	1	22	72
1-Butene ^a	21	0	76	3
1-Butene ^b	8	1	6	85
1-Pentene ^a	16	0	77	7
1-Pentene ^b	2	1	2	95
1-Hexene ^a	13	0	75	12
1-Hexene ^b	2	1	2	95
1-Octene ^a	12	0	73	15
1-Octene ^b	2	0	2	96

^a In the presence of TiCl_4 .

^b Without TiCl_4 .

stabilized in the ionic liquid. Similar isomerization reactions of olefinic double bonds in ionic liquids were recently reported by us [23]. The amount of vinyl end groups is low and almost negligible for higher olefins than ethene as their formation is energetically highly unfavourable.

The properties of the oligomers obtained in the ionic liquid differ extensively from polyethene formed in toluene under similar conditions. For comparison, ethene was polymerized by TiCl_4 (9 mmol) and EtAlCl_2 (4.5 mmol) in toluene (15 ml) at 60 °C and 55 bar. After a reaction time of 5 h and hydrolytic work up, the powdery polymer was isolated in 98% yield. This polymer showed much higher molar masses ($M_w = 97,900$ g/mol and $M_n = 1028$ g/mol) and a significantly broader trimodal polydispersity of $D = 95$. $^{13}\text{C}\{^1\text{H}\}$ NMR measurements carried out at 100 °C revealed that the polymer chain is more linear and to only 9% interlinked explaining the observed higher melting point of $T_m = 124$ °C.

4. Conclusions

The Lewis acidic (excess of 0.1 mol equivalent AlCl_3) ionic liquid [1-butyl-3-methylimidazolium] [tetrachloroaluminate] oligomerizes the linear 1-olefins ethene, propene, 1-butene, 1-pentene, 1-hexene and 1-octene, even in the presence of the scavenger ethylaluminiumdichloride to yield dimers, trimers and tetramers. If titaniumtetrachloride is added as a catalyst, branched, atactic polymers with narrow, monomodal polydispersities of $D = 1.4$ – 2.5 were isolated as waxy to oily compounds. Conversions of up to 63% after 4 h and 98% after 19 h and molar masses of $M_w = 650$ – 1620 g/mol ($M_n = 440$ – 970 g/mol) were determined independent of the monomer used. Chain end group analyses revealed that predominantly a migration mechanism leading to 1,1,2-trisubstituted double bonds occurred in a higher proportion than in toluene. Furthermore, the oligomerizations were much more selective in comparison to reactions in toluene, where under similar conditions, polyethene with a broad trimodal polydispersity ($D = 95$) was formed. However, a higher molar mass of $M_w = 97,900$ g/mol ($M_n = 1030$ g/mol) as well as a higher linearity of the polymer was obtained in toluene.

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