Norbornene-based polyolefins by cationic rare-earth metal half-sandwich catalysts

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Ethene-co-Norbornene copolymerizations were achieved by a number of half-sandwich rare-earth metal compounds of formula \([\text{Ln}((\eta^5-C_5\text{Me}_4)\text{SiMe}_3\text{R})(\eta^1-\text{CH}_2\text{SiMe}_3)_2(L))] (\text{Ln} = \text{Sc}, \text{Y}, \text{Lu}; \text{R} = \text{Me}, \text{Ph}, \text{C}_6\text{F}_5; \text{L} = \text{THF})\) and \([\text{Sc}((\eta^5-C_5\text{Me}_4)\text{SiMe}_3\text{C}_5\text{H}_4\text{N}-2)(\eta^1-\text{CH}_2\text{SiMe}_3)_2]\) activated by \([\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\). The effect of aluminum alkyls such as methylaluminoxane (MAO) or \(\text{Al}^1\text{Bu}_3\) (TIBA) was investigated. Scandium-based systems showed the best catalytic activities whereas yttrium- and lutetium-catalyst worked less efficiently indicating that catalytic activity strongly depends on the metal. The features of silyl groups of the aromatic ligand influenced both copolymer composition and molar mass distribution. Some catalysts allowed for controlled (living) copolymerization \((M_n/M_w \sim 1.2)\).

Mainly stereoirregular alternating \(\text{P(E-co-N)}\)s were obtained with the active catalytic systems. In addition, scandium catalysts were successfully exploited to prepare hydroxyl-functionalized norbornene-based copolymers and terpolymers. Co- and terpolymers with extremely high molecular mass were prepared. The most active catalytic system allowed for the \textit{in situ} copolymerization in a suspension of carbon nanotubes (CNTs) and nanocomposites of CNTs homogeneously coated with \(\text{P(E-co-N)}\) were obtained.

1 Introduction

Cyclic olefin copolymers (COCs) are specialty and engineering polyolefins based on (poly)cyclic olefin monomers and ethene or \(\alpha\)-olefins [1-2]. They have recently received great attention due to their unique properties such as high thermal stability, excellent transparency, and low moisture absorption. Among the COCs, the copolymers of ethene (E) with norbornene (N) are attractive for both cheap raw materials and smooth one-pot synthesis by addition polymerization [3]. Essentially, cationic group 4 and 10 metal homogeneous catalysts have been so far investigated. Polymerization has been fine-tuned, its mechanism investigated and the polymer microstructure/physical properties relationship established [4]. In contrast, the emerging class of homogeneous catalysts based on cationic rare-earth metals (group 3 and the lanthanides) remains rather unexplored [5]. Recent advances in organometallic chemistry of these elements has enabled the isolation of novel complexes which have shown excellent catalytic performance [6]. Regarding E-co-N copolymerization, the scandium-based catalyst \([\text{Sc}((\eta^5-C_5\text{Me}_4)\text{SiMe}_3)(\eta^1-\text{CH}_2\text{SiMe}_3)_2(\text{THF})][\text{B}(\text{C}_6\text{F}_5)_3]\) has been recently reported for its remarkable activity [7]. A number of analogous half-sandwich hydrocarbyl complexes have been prepared and characterized [8]. Herein, we report on the investigation of metal and ligand effects on catalytic behavior. In addition, the copolymerization of E with 2-hydroxymethyl-5-norbornene (\(\text{N}_2\text{OH}\)) as well as E-\textit{ter}-N-\textit{ter}-\(\text{N}_2\text{OH}\) terpolymerization were conducted by exploiting several routes for the -OH group protection [9]. Advanced functionalized norbornene-based polyolefins were successfully prepared. Functionalized polyolefins are of special interest because polar groups exercise control over important properties such as toughness, adhesion, barrier properties, surface properties, printability, miscibility with other polymers, and rheological properties, etc. [10].
Fig. 1: Half-sandwich rare-earth metal alkyl complexes. i) Complexes with piano-stool geometry $R = \text{SiMe}_3$, SiMe$_2$C$_6$F$_5$ and Ln = Sc, Y, Lu. ii) Scandium complex with monoanionic bidentate ligand.

Finally, the catalyst $[\text{Sc}(\eta^5\text{C}_5\text{Me}_4\text{SiMe}_3)(\eta^1\text{CH}_2\text{SiMe}_3)(\text{THF})][\text{B}(\text{C}_6\text{F}_5)_4]$ was tested for in situ E-coN copolymerization in a suspension of multiwalled carbon nanotubes (MWCNTs) in toluene. P(E-co-N)/MWCNTs masterbatches were achieved and nanocomposites prepared by dilution in the commercial P(E-co-N). CNTs have unique combinations of excellent mechanical, thermal, and electronic properties [11]. In the emerging technology of nanocomposites the CNTs are very attractive candidates to realize reinforced multifunctional materials [12].

2 Results and discussion

2.1 Ethene-co-Norbornene copolymerization

The copolymerizations were carried out under rigorous anaerobic/anhydrous conditions due to the tenacious Lewis base complexation, air and moisture sensitivity, as well as thermal instability, of these mono-(cyclopentadienyl) $d^{10}$ metal compounds. Thus, complexes were handled in glovebox and by Schlenck line and high vacuum techniques [13]. The copolymerization reactions were performed in toluene at atmospheric pressure in the range of temperature from 0 to 50 °C. The active species were generated by $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, which forms the cationic coordinatively-unsaturated species by abstractive cleavage of Ln-CH$_2$SiMe$_3$ bond and stabilizes it by weak anionic coordination. When exposed to monomer solutions extremely fast copolymerization occurred (complete conversion within a few minutes). The effect of aluminium compounds such as methylaluminoxane (MAO) or Al$^3$Bu$_3$ (TIBA) was studied as well [14].

Molar masses ($M_n$ and $M_w$) and molar mass distributions ($M_w/M_n$) of copolymers were determined by means of size-exclusion chromatography (SEC). Copolymers prepared without aluminium scavengers possess fairly narrow $M_w/M_n$ (under 1.5), which clearly indicates that these systems can initiate controlled (living) E-co-N copolymerization, where both termination and side-reactions do not compete with chain propagation. Kinetic experiments confirmed this feature, at least for short reaction time.

Glass transition temperatures ($T_g$s) were determined by differential scan calorimetry (DSC); $T_g$ values resulted high (even over 130 °C) and well-correlated with the norbornene content.

Copolymers compositions and microstructures were obtained by $^{13}$C NMR spectroscopy. All the systems produced stereoirregular copolymers with a marked tendency to alternation. Features of the aromatic ligand in the catalyst rule the norbornene incorporation [15].

$$[\text{LnLn(CH}_2\text{SiMe}_3)]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$$(i) (ii) $\text{P(E-co-N)}$

Fig. 2: Synthetic procedure of copolymerization. (i) Activation of complexes by abstractive cleavage of Ln-CH$_2$SiMe$_3$ bond ($X = [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$). (ii) E-co-N copolymerization by active cationic complexes.
2.2 2-hydroxymethyl-5-norbornene-based polymers

The copolymerization of E with 2-hydroxymethyl-5-norbornene (N_{OH}) as well as E-ter-N-ter-N_{OH} terpolymerization were conducted by catalyst [Sc(η^5-C_5Me_4SiMe_2C_6F_5)(η^1-CH_2SiMe_3)]_2(THF)] = 20 μmol, [Ph_3C][B(C_6F_5)_4] = 20 μmol, V(toluene) = 50 mL, T = 25 °C, pE = 1 bar, [N]/[E] = 9, aliquots sampled each minute.

Extremely high molar masses (well-above 10^5 Da) and good N_{OH} content (over 10 mol %) were achieved. In addition, P(E-ter-N-ter-N_{OH})s were prepared in a variety of compositions and with very high molar masses.

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Measurements of contact angle revealed a significant improvement in adhesion properties, even at low N$_{OH}$ content [16].

The achieved living polymerization (see paragraph 2.1) is the key to build complex architectures. Polar-apolar block polymers P(E-co-N)-b-P(E-co-N$_{OH}$) and P(E-co-N)-b-P(E-ter-N-ter-N$_{OH}$) were prepared by sequential monomer addition, exploiting the established controlled nature of these polymerization as well as the different affinity of the catalyst for monomers. The latter copolymer-block-terpolymer was prepared in higher purity. Both the block polymers exhibited self-assembling properties, as revealed by atomic force microscopy (AFM) of their cast films. These novel block polymers can be applied as compatibilizers in composite blends or in nanostructured materials.

2.3 Carbon nanotubes and norbornene-based polymer nanocomposites

The homogeneous dispersion of CNTs, especially in apolar matrices such as polyolefins, is limited by the thermodynamic drive to bundle caused by strong π−π interactions. Among the methodologies recently reported to achieve homogeneous CNTs dispersion in polymer matrices, the in situ polymerization is the most promising for polyolefins. Here, the co- and terpolymerization of E, N, and N$_{OH}$ by scandium catalysts were performed in the presence of MWCNTs in excellent yields [17]. The in situ copolymerization and the ultrasonication of MWCNT suspension led to disaggregation of MWCNT bundles. TIBA was needed as scavenger to neutralize CNT impurities. Nanocomposites with a content of about 10 wt % CNTs in P(E-co-N)$_s$, P(E-co-N$_{OH}$)$_s$ and P(E-ter-N-ter-N$_{OH}$)$_s$ as determined by means of thermogravimetric analysis (TGA) were obtained. DSC measurements showed no effect on the $T_g$s of the polymers. A fairly homogeneous coating of the nanotubes by polymers was observed by the transmission electronic microscopy (TEM) images.

P(E-co-N)-coated MWCNTs were used as pre-dispersed masterbatches and diluted in commercial TO-PAS [18] by melt-blending. Finally, compression molded films were prepared as nanocomposite manufactures whose improved mechanic properties were determined by means of dynamic mechanical thermal analysis (DMTA). TEM analysis of the films revealed that the homogeneous dispersion of carbon nanotubes was maintained after the processing.

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References

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[18] TOPAS®, which is the trademark of the commercial P(E-co-N), is the acronym for transparent olefin polymer amorphous structure.