

Macroalkoxyamines and macroRAFT agents based on polyethylene for the syntheses of polyolefin based polar block copolymers

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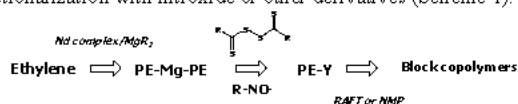
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Introduction

Despite their great successes, there are some inherent shortfalls in polyolefins materials that prevent their wider usage in many areas currently occupied by other polymers that are much more expensive and less environmentally friendly materials. Among the major drawbacks of polyolefins are their poor adhesion and incompatibility with other materials and most polymers. The incorporation of end functional groups offers an opportunity to serve as a building block for constructing multi-segmented polymers.

In organic chemistry, one of the best known transformations of a carbon-metal bond is probably the Grignard reaction where, for example, carbon-carbon bonds (R-R') are generated from the reaction of organomagnesium compounds (RMgX) with halides (R'X)¹ or stable radicals (R').^{2,3}

A large range of compounds are synthesized via this reaction type and among them alkoxyamines and dithioesters, which are of great importance as initiators and controlling agents in the field of "living"/controlled radical processes via stable free radical polymerization (SFRP) and Reversible Addition Fragmentation chain Transfer (RAFT). In the case of alkoxyamines, the organometallic compound is reacted with two equivalents of a stable nitroxide radical (R' = O-N(R1R2)).² With a view of introducing free radical initiator at the chain end of polyolefins, we plan to investigate a strategy based on the above mentioned Grignard type chemistry. Indeed, dialkylmagnesium compounds can be used as chain transfer agents (CTA) in ethylene polymerization. A pseudo-living ethylene polymerization via chain transfer reaction between dialkylmagnesium derivatives and the lanthanidocene complex (C₃Me₃)₂LnCl₂Li(OEt)₂ could be achieved (Ln=Nd⁴, Sm⁵). As chains are generated onto the catalyst, a constant and reversible transfer is operating onto the CTA where the chains are stored during the growth of other chains at the lanthanide center. As a result, the obtained long chain dialkylmagnesium compounds, Mg(PE)₂ (PE = polyethylene), of narrow molar mass distribution are excellent candidates for an end functionalization with nitroxide or other derivatives (Scheme 1).



Experimental

Materials. 2,2,6,6-tetramethylpiperidinyl-1-oxy radical (TEMPO, Aldrich, 99%) was sublimed before use. Potassium ethylxanthic acid salt (Acros, 97%) is used without any further purification for the synthesis of o,o'-diethyl dithiois[thioformate] according to the literature.⁶

Analytical techniques. High temperature SEC analyses were performed using a Waters Alliance GPCV 2000 chromatograph equipped with three columns (2 Styragel HT6E and 1 Styragel HT2). Samples (1 mg.mL⁻¹) were eluted with trichlorobenzene with a flow rate of 1 mL.min⁻¹ at 150°C. Online detection was performed by refractometry and a viscosimetry measurements using Waters equipments. High-resolution liquid NMR spectroscopy was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for ¹H and 100.6 MHz for ¹³C. Spectra were obtained with a 5-mm QNP probe at 363K. Polymer samples were examined as 10-15 % (w/v)

solutions. A mixture of tetrachloroethylene (TCE) and perdeuterobenzene (C₆D₆) (2/1 v/v) was used as solvent. Chemical shift values (δ) are given in ppm in reference to internal tetramethylsilane (TMS).

Polymerization and functionalization procedures. Ethylene polymerization was carried out under atmospheric pressure in toluene according to literature.⁵ A mixture of chloronodimocène complex (5.46.10⁻² mmol) and n-butylmagnesium (BOMg, 0.5 mmol) in toluene (5 mL) was stirred for 1 h at room temperature. The resulting clear blue solution was then transferred via syringe into the reactor under stirring. At the end of the polymerization, the resulting mixture was poured into 200 mL of methanol. The polymer was collected by filtration, washed with methanol (300 mL) and dried in vacuo at room temperature for 12 h. For functionalization, prior the addition of methanol, a solution of TEMPO or other compounds in toluene (5 mL) was added and the resulting mixture was stirred at 80°C for 2h.

Results and discussion

Reaction of Mg(PE)₂ with nitroxides.⁶ After checking the controlled characteristics of the ethylene polymerization catalytic system, the functionalization of the polyethylene chains by reacting a stable nitroxide, namely the 2,2,6,6-tetramethylpiperidinyl-1-oxy radical (TEMPO) with PE-Mg-PE was investigated. In that respect, at the end of the polymerization, a solution of TEMPO in toluene was simply added to the medium at 80°C (molar ratio TEMPO / Mg = 4/1) and the resulting mixture was stirred for two hours. The recovery of the polymer by precipitation in methanol gave a white powder which was analyzed by ¹H and ¹³C NMR. The obtained spectra are typically those of a polyethylene that is usually prepared with the used catalytic system except for the presence of resonances that are attributable to end groups derived from TEMPO. The use of these analytical techniques allowed to quantify the functionalization efficiency. 74% of the PE chains were end-functionalized.

Reaction of Mg(PE)₂ with disulfides.⁷ Based on the same strategy, we also successfully investigated the introduction of dithioesters based end functions such as dithiocarbamate, dithiocarbonates, dithioesters, and trithiocarbonates.

Controlled Radical Polymerizations using functional polyethylenes. As the use of a PE-TEMPO macroalkoxyamine in a free radical polymerization would require a high temperature (more than 180°C to reversibly cleave the PE-TEMPO bond), new original nitroxides (named DD1, DD2) were designed, synthesized and used to get appropriate functional polyethylenes for these purposes. Controlled radical polymerization of butyl acrylate using PE-DD1 and PE-DD2 was successful and the production of a poly(ethylene-*b*-butyl acrylate) demonstrated.

Among the different thiocarbonyl thio end capped polyethylenes, PE-trithiocarbonates were the best candidates to perform under RAFT control the polymerization of butyl acrylate producing again a poly(ethylene-*b*-butyl acrylate) block copolymer.

Conclusion

In conclusion, alkoxyamine and thio thiocarbonylated terminated polyethylenes can easily be prepared and can mediate the controlled radical polymerization of polar monomers for the synthesis of original block copolymers incorporating a polyolefin block.

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