



## Copolymerization of ethylene with a vinyl ether bearing a fluorinated group

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### ABSTRACT

The copolymerization of ethylene (E) with 1*H*,1*H*,2*H*,2*H*-perfluorodecyl vinyl ether (FAVE8) by oxidative addition of salicylaldimine ligand to bis(1,5-cyclooctadiene)nickel(0)/methylaluminoxane (MAO) at room temperature and at different ethylene pressures is reported. The homopolymerization of ethylene is known to be highly active with this catalyst in contrast to the fluorinated vinyl ether which does not homopolymerize. The copolymerization of E with FAVE8 led to linear poly(E-co-FAVE8) statistic copolymers that were characterized by means of various techniques. The obtained copolymers, analyzed by FT-IR and solid state NMR spectroscopy, showed a small incorporation of the fluorinated vinyl ether. Three copolymerization reactions were investigated with different ethylene pressures (5, 10 and 50 bar) and the copolymer compositions indicated that the content of FAVE8 units depends on the ethylene pressure. The lower this pressure, the higher the content of such a fluorinated comonomer and for a 50 bar-pressure, no FAVE8 was incorporated. Thermogravimetric and differential scanning calorimetry analyses of these resulting copolymers exhibited high thermal stability, the thermal degradation starting from ca. 300 °C whereas high melting point ( $T_m = 129$  °C) were achieved with these copolymers. Original films processed from these poly(E-co-FAVE8) copolymers illustrated hydrophobic and oleophilic characters as evidenced by water and diiodomethane contact angles of 104° and 49°, respectively.

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## 1. Introduction

The direct synthesis of functionalized polyethylenes (PE) by metal-catalyzed insertion copolymerization of ethylene (E) and polar vinyl monomers is an attractive goal. This approach to copolymer synthesis requires the development of new catalysts, likely based on late transition metals, which are tolerant of the functional groups on the polar monomer and the growing copolymeric chain. In this context, Brookhart's group [1,2] discovered ( $\alpha$ -diimine) PdR<sup>+</sup> species that catalyzed the copolymerization of alkyl acrylates with olefins to highly branched copolymers with acrylate units located primarily at branch ends. Pugh's [3] and Mcintosh's [4] teams reported that neutral (phosphine-sulfonate)PdR species generated in situ catalyzed the copolymerization of E with acrylate to linear copolymers with significant in-chain acrylate incorporation. Luo and Jordan [5] reported the (R-diimine)PdMe<sup>+</sup> catalyzed copolymerization of olefins and silyl vinyl ethers. However, the resulting copolymers were highly branched with comonomer units located mostly at branch ends as evidenced by <sup>1</sup>H NMR spectroscopy. Marconi et al. [6] reported the discrete catalyst (PO-OMe)PdMe(pyridine)

copolymerized E and alkyl vinyl ethers to linear copolymers that contain in-chain –CH<sub>2</sub>CH(OR)– comonomer units. In addition, Runzy et al. [7] found neutral palladium(II) phosphinesulfonate catalysts were stable toward carboxylic acid moieties and enabled direct linear copolymerization of E with acrylic acid.

However, literature survey reveals that palladium sulfonated aryl phosphines were able to copolymerize E with many comonomers such as acrylates, norbornenes, vinyl ethers, styrenes, vinyl ketones, vinyl esters, acrylonitrile, vinyl fluoride, acrylamides and N-vinyl amides [1–8]. So far, more attention has been devoted to palladium derivatives which have been employed as olefins and polar vinyl monomers copolymerization catalyst, whereas nickel-based complexes received considerably less attention for this investigation. In this field, only a few results have been reported: Carlini et al. [9] disclosed the preparation of poly(E-co-vinyl ethers) copolymers with a nickel(II) salicylaldimine catalytic system. In addition, the same research team reported that these catalysts and their subsequent activation by MAO gave catalytic systems able to copolymerize ethylene with methyl methacrylate (MMA) to give functionalized high molecular weight linear polyethylene (PE) samples with a rather low content of polar co-units (3–6%) and with a quite good productivity [10,11]. However, it has been known that poly(E-co-polar vinyl monomers) copolymers produced a wide variety of applications ranging from oils and waxes to solid copolymeric products, with improved optical properties [7] as well as showing

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improved stiffness, yield point and ultimate tensile strength [12]. Besides these copolymers, many fluorinated (co)polymers have also been studied for their peculiar properties [13–15]. The synthesis of functionalized polyolefins by insertion copolymerization of olefins and polar vinyl monomers bearing fluorinated group is a challenging and most desirable goal. As a matter of fact, fluoropolymers are well-known for their high-performance features, i.e., heat and chemical resistance, low refractive index, low surface energy, and durability [13–15], and therefore can be involved in a wide range of applications, e.g. paints, actuators, transducers, fuel cell membranes, optical fibers, thermal and surface active coatings, gaskets, O-ring, insulating wires, high performance elastomers, and textiles finishings. An ongoing challenge in Polymer Science is the preparation of materials with specific surface properties which differ from those of the bulk, for example, hydrophobicity, oleophobicity, chemical resistance, adhesion, or biocompatibility, while retaining the advantageous mechanical properties of the bulk polymer [16]. Concerning these applications, research trend has also been shifted toward the synthesis of poly(olefins-co-fluorinated monomers) copolymers to enable improved solubility and processing. The incorporation of halogens into polyolefins influences many key polymer properties, including solvent resistance, gas barrier properties, adhesion, flammability, toughness, and thermal properties [13–15,17–25]. However, several studies encompass insertion of fluoro monomers with olefins and these copolymers exhibited interesting properties in terms of hardness, cross-cut adhesion, chemical inertness, and surface properties [25–36]. Notwithstanding, few studies, particularly on the synthesis of poly(E-co-fluorinated monomers) copolymers have been reported, including two main thermoplastics, based on chlorotrifluoroethylene (CTFE), ECTFE and tetrafluoroethylene (TFE), ETFE, commercialized by the Ausimont and Dupont companies under the HALAR<sup>®</sup> or TEFZEL<sup>®</sup> trademarks, respectively [37,38]. Interestingly, both these copolymers are alternating [39]. Copolymers of E and TFE have been known since 1946 [40] have an excellent balance of physical, chemical and electrical properties, and are melt processible [39]. In addition, Takakura's group [37,41] claimed that these copolymers were excellent in heat and chemical resistances and were widely used as a material suitable for corrosion (e.g. as resistant lining or corrosion resistant containers). They provided a molding method for a ETFE copolymer powder, whereby the surface smoothness of the coating film obtained or remarkably improved. ETFE resins have been manufactured by DuPont, Asahi Glass, Daikin, Hoechst (now 3M/Dyneon) and Ausimont (now Solvay-Solexis), under the Tefzel<sup>®</sup>, Aflon<sup>®</sup>, Neoflon<sup>®</sup>, Hostaflon<sup>®</sup> and Halon<sup>®</sup> trade names, respectively.

Worldwide production in 1994 was about 2900 metric tons selling while the price range was about US\$ 24–44 per kilogram. Weng et al. [42] reported the copolymerization of ethylene with vinyl fluoride using (phosphine-sulfonated)Pd(Me)(py) catalysts that led to linear fluorinated polyethylene.

So far, no data have been reported on the copolymerization of E with polar vinyl monomers bearing fluorinated group. In addition, to the best of our knowledge, fluorinated (co)polymers are usually synthesized by radical copolymerization [13–15] and a few from palladium-based complexes [14].

However, nickel-based complexes are totally new in the field of the copolymerization of non fluorinated olefins with fluorinated monomers. In this context, for the first time, this article reports the copolymerization of E and polar vinyl monomer bearing fluorinated group such as 1*H*,1*H*,2*H*,2*H*-perfluorodecyl vinyl ether (FAVE8) by oxidative addition of 3,5-dinitro-*N*-(2,6-diisopropylphenyl)salicylaldimines to a nickel (0) precursor such as bis(1,5-cyclooctadiene)nickel(0) [Ni(cod)<sub>2</sub>], which gives rise to the corresponding (η<sup>1</sup>,η<sup>2</sup>-cycloocten-1-yl)salicyladimate nickel (II) complex (I) when activated with MAO (Scheme 1 [43]).

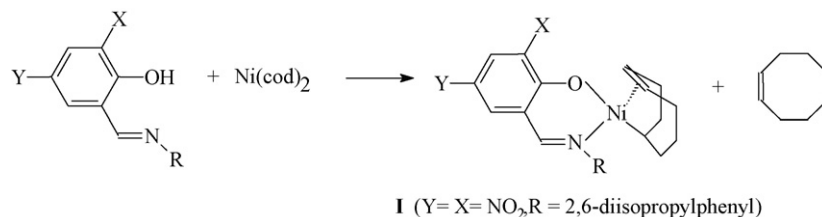
It is interesting to note that other Ni catalysts [(α-diimine)-Ni(II)/MAO systems] have been reported to be active in homopolymerization of alkyl vinyl ethers to give the corresponding atactic polymers, although characterized by rather low molecular weights [44]. On the other hand, Ni systems are completely inactive in homopolymerization of FAVE8. Indeed, the catalytic system I/MAO is able to polymerize with a high activity not only ethylene to a high molecular weight linear PE [45,46] but also polar monomers, such as MMA [47]. Therefore, due to its fair stability, facile synthesis and low cost, this complex is expected to be the most suitable candidate for this type of reaction.

Another goal of this present article, deals with the insertion of perfluoroalkyl dangling groups (from FAVE8) that should induce better surface properties.

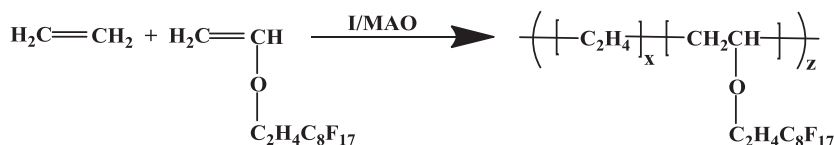
## 2. Results and discussion

### 2.1. Copolymerization of ethylene with 1*H*,1*H*,2*H*,2*H*-perfluorodecyl vinyl ether (FAVE8)

Preliminary homopolymerization experiments of FAVE8, either by MAO alone or by the I/MAO catalytic systems, in toluene solution (with an Al/Ni ratio of 15 mol/mol) did not give any polymer yield, at least at room temperature, even after 96 h of reaction.



**Scheme 1.** Synthesis of nickel (II) salicyladimate from oxidative addition of 3,5-dinitro-*N*-(2,6-diisopropylphenyl)salicylaldimines to bis(1,5-cyclooctadiene)nickel(0) [Ni(cod)<sub>2</sub>] [43].



**Scheme 2.** Synthesis of poly(E-co-FAVE8) copolymers based on ethylene (E) and 1*H*,1*H*,2*H*,2*H*-perfluorodecyl vinyl ether (FAVE8).

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