



# Functional polyethylene with regularly distributed ester pendants via ring-opening metathesis polymerization of ester functionalized cyclopentene: Synthesis and characterization



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## ABSTRACT

A new series of functional polyethylene (PE) with ester pendant ( $-\text{COOR}$ , R = methyl, ethyl, *n*-propyl, *n*-butyl, *n*-octyl, *n*-dodecyl, *n*-tetradecyl and *n*-hexadecyl) on every five main chain carbons were prepared via ring-opening metathesis polymerization (ROMP) of COOR functionalized cyclopentene catalyzed by a ruthenium-based catalyst and subsequent hydrogenation of the ROMP products. High monomer conversions (70–80%) were achieved in all the ROMP reactions. Chain structure, molecular weight and molecular weight distribution (MWD) of the ROMP products and hydrogenated polymers were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and GPC, which showed regular distribution of the COOR pendants along the main chain, moderate molecular weight and narrow MWD. Thermal properties and side chain crystallization behaviors of the functional PEs were investigated by differential scanning calorimetry (DSC). Glass transition temperature ( $T_g$ ) of the polymer decreased for nearly 30 °C when R of the pendant COOR was enlarged from methyl to *n*-octyl, and the new polymers showed lower melting temperature ( $T_m$ ), higher side chain crystallinity ( $X_c$ ) and more precise side chain lamellar crystal thickness ( $l_c$ ) as compared with corresponding polyacrylates carrying the same side alkyl. The new polymers exhibited moderate thermal stability.

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## 1. Introduction

Polyethylene (PE) has been widely used as commodity polymeric materials for its easily available raw material and highly efficient polymerization techniques [1–3]. Furthermore, for its simple chain structures, PE-based polymers are ideal model polymers for studying structure–property relationships. Not surprisingly, well-defined polyethylene and copolymers containing PE segments have attracted increasing attentions in functionalization of polyolefins. Especially, well-defined ethylene-based copolymers present more opportunities to integrate various potentially advantageous performances as compared to corresponding ill-defined copolymers or homopolymers of similar composition [4]. In addition, knowledge of structure-properties relationship on these precision PE would provide useful references for designing and synthesizing novel polyolefins, including chain stacking [5],

crystallization behaviors [6,7], and thermal properties [8,9].

Ring-Opening Metathesis Polymerization (ROMP) of cyclic olefins such as cyclopropene [10], cyclobutene [11,12], cyclopentene [13–16], cyclohexene [17], cycloheptene [18], cyclooctene [19–22], and norbornene [23–27], etc. using ruthenium-based catalysts, represents an equally powerful method of preparing perfectly linear polyethylene and its copolymers as compared to acyclic diene metathesis polymerization (ADMET) and other newly discovered synthetic methods of controlling sequence distribution [28–33]. Ruthenium-based catalysts have been preferentially chosen to initiate the metathesis polymerization for its remarkable catalysis efficiency, thermal and chemical stability [34,35], and excellent tolerance toward a series of functional groups like hydroxyl [36], ester [37], thioether [30], etc. [38,39]. Recently, high molecular weight polymer containing polar groups was synthesized by ROMP for application as oil additive to improve transportation safety [40], showing bright prospects of new functional polyolefins. Accordingly, exploring other novel materials based on existing resource should be of great significance both in academia and industry.

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