Innovating Polyethylene with Cyclic Side Chains: Synthesis, Structure, and Properties

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The incorporation of side chains commonly referred to as short chain branches (SCBs) into the linear backbone of polyethylene (PE) significantly influences key polymer properties such as crystallinity, density, and mechanical performance. Ethylene polymerization via coordinative Ziegler–Natta (ZN) catalysis typically yields highly linear macromolecular structures capable of forming crystalline domains. The introduction of SCBs disrupts this regular packing, thereby reducing the degree of crystallinity. Modulation of the structure and concentration of SCBs enables the tuning of material properties to suit specific applications.[1] Previous investigations have demonstrated that branched comonomers, such as iso-hexene and neo-hexene, exert a greater disruptive effect on crystalline structure compared to their linear analogue, n-hexene.[2] Building on these findings, this study explores the potential of cyclic SCBs characterized by increased steric hindrance to elicit similar or enhanced effects. To this end, three cyclic comonomers (depicted in Figure 1) were evaluated for their feasibility in ethylene copolymerization.

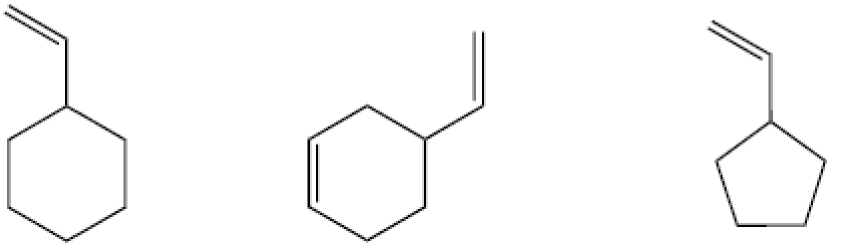
vinylcyclohexane 4-vinylcyclohex-1-ene vinylcyclopentane

Figure 1 Comonomers used to introduced cyclic SCBs in PE copolymers.

Successful copolymerization of vinylcyclohexane and 4-vinylcyclohexene-1 with ethylene has been previously documented using a variety of catalytic systems, including metallocenes and ZN catalysts.[3],[4] The current study compares the kinetic behavior of these copolymerizations including catalyst activation and deactivation dynamics with those observed in the homopolymerization of ethylene. Additionally, the resulting polymers were characterized in terms of their molecular weight distributions and thermal properties, which are affected by the nature of the incorporated comonomers. Variations in melting temperatures and enthalpies reflect alterations in crystalline content induced by the cyclic side chains.

For comparative purposes, a series of copolymerizations involving ethylene and n-butene was also performed. These conventional copolymers, containing linear and relatively shorter SCBs, serve as reference materials to contextualize the influence of cyclic branching on polymer structure and properties.

Quantitative ^{13}C nuclear magnetic resonance (NMR) spectroscopy confirmed that a minor fraction of the respective cyclic comonomers was successfully incorporated into the polymer backbone, further supporting the structural modifications observed.

References

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