

Terminal functionalization of polypropylene via the Alder Ene reaction

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A terminally anhydride functionalized polypropylene was synthesized via the Alder Ene reaction from a low molecular weight amorphous polypropylene. A Lewis acid, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, was found to catalyse the reaction, thereby improving anhydride content in the polymer for reaction conditions comparable to those in an extrusion environment, i.e. elevated temperature and short residence time. The reaction was carried out at 230°C for 5 min in the presence of TEMPO, which acted as a free radical trap, preventing maleic anhydride from being grafted onto the backbone of the polypropylene. The product was characterized by several techniques, including FTi.r. and n.m.r., to provide evidence of the anhydride location on the chain. Several runs of varying catalyst concentration have shown that an optimum in anhydride incorporation onto the polypropylene exists. Examination of the system kinetics has shown that the overall order of the reaction remains second-order despite the presence of a catalyst.
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INTRODUCTION

Polypropylene has over the past few years shown the most rapid growth of practically any polymer on the market¹. The entrance of this material into non-conventional engineering markets such as the automotive industry has brought with it both intense interest and difficulties. The chemical inertness of polypropylene, so often exploited in conventional commodity products such as bottles and films, restricts its use in more demanding engineering products which often require a blending of polymer characteristics to meet customer specifications. In recent years, reactive modification of polypropylene in an extruder via free radical grafting has become a vigorously pursued post-polymerization method for incorporating functionality into the material^{2–9}. Collectively researched in both academia and industry, it has been found that the random covalent attachment of a comonomer onto the backbone of the polymer by a radical mechanism is often accompanied by degradation. Maleic anhydride functionalization of polypropylene has received intense interest for the improved compatibility with hydrophilic systems which the functionality imparts to the polymer. Interest in maleic anhydride has been primarily due to the difficulty in homopolymerization of this comonomer during free radical grafting. The generation of poly(maleic anhydride) chains has been theorized to proceed through a cationic mechanism which relies on the formation of an excimer^{4–6}. The actual presence of poly(maleic anhydride) segments (grafted or free) under standard processing conditions has been the subject of debate in the literature for some time^{4–6,8,10}. Contrary to chain backbone modification, end-group reactions are not generally applicable to polyolefins since the macromolecules lack any reactive functionality. However,

researchers have studied several different chemistries to functionalize polypropylene terminally^{11–16} using the only functional group present, a 1,1-disubstituted double bond (vinylidene). The functional groups produced by these reactions have included anhydride, silane, thiol, epoxide, borane and its hydroxyl derivative, and carboxylic acid species. End-group modifications have been carried out in both the melt and solution. Among the chemistries explored for end-group modification, the Alder Ene reaction¹⁷ appears to be particularly suited for functionalization of polymers in the melt phase.

The Alder Ene reaction, sometimes referred to as a pericyclic reaction due to the 6-centre transition intermediate resulting from its concerted mechanism, involves the interaction of an *ene* (an unsaturated species with an allylic hydrogen available) and an *enophile* (an unsaturated species usually with neighbouring electron-withdrawing groups) forming a 1:1 adduct. The intermolecular reaction between the *ene* and *enophile* requires elevated temperatures in the range of $200\text{--}600^\circ\text{C}$ ¹⁸ where an optimum exists, after which the retro-Ene¹⁹ reaction dominates. A series of papers²⁰ on the Ene reaction between maleic anhydride and polyisobutylene (which is chemically similar to polypropylene with respect to the environment of the terminal vinylidene functionality) provided several important insights into this reaction. Two isomer products were generated from the terminal vinylidene species as shown in *Figure 1*, with the *exo* species (*a*) being dominant compared to the *endo* species (*b*). A small percentage of the original vinylidene proceeded via isomerization to an internal (*endo*) vinyl prior to coordinating with a maleic anhydride, thereby sterically inhibiting the Ene reaction. Finally, the pendant (*exo*) vinyl resulting from the reaction allowed a second maleic anhydride to attach in the case of a small model molecule, though such a reaction has been determined to be insignificant in macromolecules due to steric hindrance²¹.

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