

## ABSTRACT

The main objective of the thesis is to study the homo- and copolymerization of selected bicyclic olefins using Ziegler-Natta catalysts. The bicyclic olefins used in the study are, (1) 2-allylnorbornane which is an  $\alpha$ -olefin bearing a bicyclic ring on the carbon  $\alpha$  to the double bond, and (2) 5-vinyl-2-norbornene which is an  $\alpha,\omega$ -diene consisting of one endocyclic and one exocyclic double bond.

The first part of the work deals with the homopolymerization of 2-allylnorbornane using conventional Ziegler-Natta, and homogeneous metallocene catalysts. The use of the conventional Ziegler-Natta catalysts gave rise to a solid polymer, namely poly(2-allylnorbornane). This was fractionated into a fraction soluble in xylene at 130°C and another insoluble in xylene at 130°C. The xylene insoluble fraction had a  $T_m$  of 355°C. The insoluble nature and high melting temperature of the polymer are attributed to the presence of the bicyclic group. The homogeneous metallocene/MAO catalyst system gave only oligomers presumably due to increased  $\beta$ -hydrogen elimination reactions.

Copolymerization of ethylene with 2-allylnorbornane was studied using  $\text{TiCl}_4/(\text{iso-Bu})_3\text{Al}$ , a conventional Ziegler-Natta catalyst, and  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ , a homogeneous metallocene catalyst. The copolymers were characterized by IR, NMR, TGA, DSC, GPC and solution viscosity. Based on these analyses and the value of reactivity ratios, it was concluded that the copolymers obtained using  $\text{TiCl}_4/(\text{iso-Bu})_3$  catalyst are heterogeneous with a blocky distribution of comonomers, whereas, those obtained using  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  catalyst are homogeneous with a random distribution of comonomer units. The thermal properties of both these sets of copolymers were compared with ethylene 4-methyl-1-pentene copolymers (their acyclic analogue), synthesized under identical conditions, in order to study the specific effect of the bicyclic pendant. It was found that at similar mol% incorporation of comonomers (2-allylnorbornane or 4-methyl-1-pentene), the

decrease in melting point and crystallinity of the copolymer were the same. This is attributed to the fact that, contrary to expectations, the space filling characteristics of the two pendant groups (norbornyl or isopropyl) is not significantly different.

Copolymerization of ethylene with 5-vinyl-2-norbornene was studied using  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  catalyst. A regioselective insertion of the endocyclic double bond of the comonomer into the growing polymer chain was observed leaving the vinyl bond as a pendant.

The poly(ethylene-co-5-vinyl-2-norbornene) containing pendant vinyl group was functionalized to epoxy and hydroxy group containing polymer using standard organic transformations. Further the epoxy group containing polymer was used in a "grafting onto" coupling reaction with living poly(styryllithium) resulting in poly(ethylene-co-5-vinyl-2-norbornene)-graft-polystyrene.