Copolymerization of Norbornene with Ethylene: a High-resolution Liquid NMR, DSC and Solid State NMR Study

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Abstract: In this paper, we report the monomer reactivity on the copolymerization of norbornene and ethylene. The reactivity ratios for ethylene (M₁) and norbornene (M₂) are 18.5 and 0.035, respectively. Different copolymerization conditions can produce COC with different microstructures. A ¹³C NMR shift assignment in pentad sequences in copolymers has been obtained. More isolated polynorbornene or a micro-block length can be obtained using a low Zr/Al catalyst/co-catalyst ratio and at a lower NB/ethylene feed ratio. The T₁p c decay curve shows two component decays in all resonance peaks. These two component decays come from different norbornene microstructures, while the block and alternative have similar T₁p c values.

Keywords: Cyclo olefin copolymer (COC), Monomer reactivity ratio, Solid state NMR, Spin-lattice relaxation time (T₁p c).

Introduction

The copolymerization of norbornene with ethylene leading to cyclo olefin copolymer (COC) and its characteristics has been reported in the literature recently [1-9]. These COC products possess high Tg, high transparency, and a high refractive index, and they have potential applications for electrotic and optical devices [4]. Polymer microstructure has great influence on the properties of the product, which are closely tied to the kinetics of the copolymerization reaction governed by the monomer, catalyst, and reaction conditions. The monomer reactivity ratio (r₁ and r₂) provides direct information on the competition between commoners with a given catalyst.

Previous studies on the reactivity ratio in a COC system by a metallocene catalyst indicated that the cyclo olefin has a low reactivity ratio and an alternative microstructure [9-17]. The reactivity ratio of a copolymer is crucial to understanding the copolymer microstructure and its relationship to the final properties. For example, a block copolymer usually has a relatively higher decomposing temperature (Tg) than a random copolymer or a statistical random copolymer with comparable molecular weight.

A living polymerization system has active centers with long half time. When an active center fails to react with the monomer, it still has the chance to react with a monomer added later. The feed sequence can affect the microstructure of the copolymer and the result is either a more block-like or a more random-like structure.

Knowledge of the copolymer chain sequence reveals important information regarding the chain growth mechanism and kinetics during copolymerization. An unambiguous structure quantification of the COC by the solution NMR has not yet been achieved due to its structural complexity. Furthermore, epimerization of NB may give rise to endo or exo structures in addition to erythro (E) and threo (Z) structures and may cause additional complication in the interpretation of NMR spectra. Fortunately the strong internal strain in NB bonding makes larger chemical shift differences in the pentad sequence that allow for a clearer detection of the pentad sequence. These results are then compared with the conventional characterization method using block, alternate, and isolate NB segments. The effect of catalyst structure on the reactivity ratio

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Experimental

1. General polymerization procedure

COC was polymerized from norbornene and ethylene using an ansa-metallocene catalyst Ethylidenyl\(\text{ZrCl}_2\) (from Alderich Chemical Co., USA) and MAO co-catalyst(10 wt% in toluene, from Albemarle Chemical Co., USA) [1-4]. The polymerization temperature was controlled at 66 °C using a catalyst/co-catalyst ratio from 3000 to 7000 and the ethylene pressure was maintained at 19-21 psi. Total volume of the system was 60-65 mL during the 2 hrs of polymerization time. The amount of metallocene catalyst was kept at ca. 2 mg. 10-ML acidic methanol was used to terminate the polymerization. The polymer was precipitated by adding an excessive amount of acetone non-solvent and then dried for 8 hrs at 50 °C in a vacuum.

2. Characterization of polymers

\(\Delta\text{C}^1\) and DEPT (135°) experimentals on poly-