CHAPTER I

INTRODUCTION

Nowaday, the production of polyolefins has grown to a huge industry, and the amount of polyolefins produced is about 46 million metric tons per year over the world [1]. Especially, polyethylene is the world's largest volume bulk plastic with annual consumption. Polypropylene is the third-ranked bulk plastic with annual consumption. These two polyolefins alone account for 35% of all thermoplastics and elastomers [2].

Plastics have an influence on life at nearly every level in society today. Their resistance to corrosion, and tremendous technological flexibility has enabled them even to supersede and replace metals in the construction of many household tools and creature comforts [3]. For the above reason, the polyolefin process technologies were widely interested and developed in terms of economics, versatility, safety and environmental efficiency.

In 1933, polyethylene was discovered by Fawcett and Gibson [4-5]. Karl Ziegler [6-7], Guilio Natta [8-9] and Paul Hogen [10] discovered the revolutionary first-generation Ziegler-Natta trasition metal catalyst system in 1953. The second-generation $MgCl_2$ and/or donor supported Ziegler-Natta transition metal catalyst system, which was at least 100 times more active, led to the development of the low-pressure polymerization process for polyolefins and synthetic elastomers [11]. This revolutionary catalyst system resulted in the development of simplified gas-phase low-pressure polymerization plant operation without the need for the removal of residual trace catalyst from the polymer. It was estimated that more than 36 billion kilograms of polymers were produced globally with the Ziegler-Natta transition metal catalyst system in 1997 [4].

However, the Ziegler-Natta catalyst has the property to provide polymers with a wide molecular weight distribution (MWD) and composition distributions due to

multiple active sites (multi-site catalysts, MSC). In contrast, Metallocene catalyst which can control composition distribution, MWD, incorporation of various comonomers, and stereoregularity, was developed for polyolefin production [1]. The metallocene catalysts are generally called single-site catalysts because of the equality of each catalyst site.

The name 'metallocene' was coined in the early 1950s as a more elegant replacement for the term 'iron sandwich' describing dicyclopentadienyliron, a compound of iron and cyclopentadiene-$(C_5H_5)_2Fe$ or Cp_2Fe. Its structure was explained by Geoffrey Wilkinson and Ernst Otto Fisher in 1954 as an iron atom sandwiched between parallel planar cyclopentadienyl groups. The name is now applied generally to similar organometallic structures, including those having substituted cyclopentadienyl (Cp) groups such as indene and fluorene, and those with only one Cp group. The most common metal centres used in metallocene catalysts for olefin polymerization are Zr, Ti and Hf [2]. Walter Kaminsky's group discovered that small additions of water greatly increased the metallocene catalyst's activity when trimethyaluminium (TMA) was used as the cocatalyst [12-13]. Subsequent studied showed that this activity resulted from the formation of methyaluminoxane (MAO) by the hydrolysis of TMA. The active catalytic site formed is an ion pair: a metallocene cation that is coordinately unsaturated and is stabilized by a bulky, non-coordinating MAO anion. Titanocenes, zirconocenes or hafnocenes, used with MAO cocatalyst made by the careful hydrolysis of TMA, form extremely active polymerization catalysts. This activity is higher than activity of conventional Ziegler-Natta catalysts.

Metallocene catalysts have been used to produce polyolefins commercially since 1991. In addition, metallocene can readily polymerize bulky monomer such as styrene and norbornene to make novel polymer with physical properties competitive with high performance engineering plastics such as nylon polycarbonates and polyesters [2]. However, the polymer yield produced from metallocene catalyst, although very much higher, was still too low, and catalyst system costs remained too high because of high Al:M (M = Ti, Zr, Hf) ratios for using olefin polymerization.

Recently, the Al:M (M = Ti, Zr, Hf) ratios have been substantially reduced using non-aluminoxane cocatalysts or half-metallocene catalyst but activity was still high. With their extreme activity, these new systems are cost competitive with current Ziegler-Natta and other catalyst systems for polyolefins [2]. In fact, overall cost contribution of metallocene catalysts to polymer manufacturing costs will be lower than the costs of current Ziegler-Natta system. Additionally, new polymers which could never have been produced by conventional Ziegler-Natta catalysts, i.e. syndiotactic polystyrene, long chain branched polyolefins, cycloolefin polymer and styrene copolymer can be obtained by metallocene catalysts.

Beyond the improvements in activity and the reduction of the high cost of the cocatalyst, these catalysts also offer opportunities to make polymers with properties well beyond the capabilities of any previously-known technology [1]. The study of metallocene catalyst synthesis for olefin polymerization is one of the areas of greatest interest. The results of this study will increase our knowledge on the metallocene catalyst technology in olefin polymerization. Development of new catalyst systems is the greatest challenges and lead to a wide range of new polymeric materials.

1.1. The objective of the thesis

To study the preparation stepwise of monocyclopentadienyl-metallocene catalyst with using styrene polymerization.

1.2. The scope of the thesis

1. Study and prepare the catalyst system of monocyclopentadienyl-metallocene compound with methylaluminoxane compound. Monocyclopentadienyl-metallocene catalyst which is the (η^5-indenyl)titaniumtrichloride compound was synthesized and then reacted with methylaluminoxane cocatalyst.

2. Study the properties of synthesized catalyst with using Nuclear Magnetic Resonance (NMR), Electron Spin Resonance (ESR).

3. Study the styrene polymerization with using trimethylaluminum (TMA).

4. Investigate the optimum conditions in the polymerization of styrene with IndTiCl$_3$/MAO catalyst system as follows.

4.1. Examine the effect of polymerization temperature on polymer yield and catalytic activity by varying the temperature between 30-70°C.

4.2. Determine the effect of catalyst concentration on polymer yield and catalytic activity by fixing the constant Al/Ti mole ratio.

4.3. Examine the effect of catalyst/cocatalyst mole ratio on polymer yield and catalytic activity by varying the catalyst/cocatalyst mole ratios between 1:1,000 and 1:5,000 with fixed concentration of catalyst.

5. Study properties of prepared polystyrene with using Infrared Spectrophotometer (IR), etc.