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Copolymerization of Ethylene/1-Tetradecene Viapoly (Styrene-Co-Divinylbenzene)-Supported Cp_2ZrCl_2/MAO Catalyst

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บทคัดย่อ

ศึกษาการใช้พอลิสไตรีนโคไดไวนิลเบนซีนเป็นตัวรองรับสำหรับตัวเร่งปฏิกิริยา Cp_2ZrCl_2/MAO เพื่อโคพอลิเมอร์ไรเซชันของเอทิลีน/1-เตตระเดกซีน มีวัตถุประสงค์เพื่อศึกษาผลของอัตราส่วนระหว่างเอทิลีนต่อ1-เตตระเดกซีนที่มีผลต่อความว่องไวของตัวเร่งปฏิกิริยาและคุณสมบัติของพอลิเมอร์ที่ได้ ปฏิกิริยาโคพอลิเมอร์ไรเซชันของเอทิลีน/1-เตตระเดกซีนจะถูกสังเคราะห์ในถังปฏิกรณ์เซมิแบทที่เป็นโลหะเหล็กกล้าไร้สนิทขนาด 100 มิลิลิตรซึ่งถูกกระตุ้นด้วยตัวเร่งปฏิกิริยาร่วม MAO ที่อุณหภูมิ 70 องศาเซลเซียลและทำการป้อนเอทิลีนที่ความดัน 6 ปอนด์ต่อตารางนิ้วที่ความเข้มข้นของโคมอนอเมอร์แตกต่างกัน ผลจากการวิเคราะห์ด้วยการสแกนนิงอิเล็กตรอนไมโครสโคปี พบว่าชนิดของตัวว่องไวจะอยู่บนพื้นผิวและกระจายตัวสม่ำเสมอบนพื้นผิวอนุภาค โคพอลิเมอร์ไรเซชันจะให้ความว่องไวที่สูงกว่าโฮโมพอลิเมอร์ไรเซชัน นอกจากนี้ยังพบว่าความว่องไวจะเพิ่มขึ้นเมื่ออัตราส่วนของเอทิลีน/โคมอนอเมอร์เพิ่มขึ้น คุณสมบัติของโคพอลิเมอร์ที่ผลิตได้ถูกตรวจสอบโดยใช้สแกนนิงอิเล็กตรอนไมโครสโคปี นิวเคลียร์แมกเนติกเรโซแนนซ์และดิฟเฟอร์เรนเชียลสแกนนิงคาลอรีเมทรี พบว่าโคพอลิเมอร์มีการกระจายตัวเหมือนกันโดยส่วนใหญ่จะเป็นแบบ [EEE] และความเป็นผลึกของโคพอลิเมอร์จะลดลงเมื่อความเข้มข้นของโคมอนอเมอร์เพิ่มขึ้น

ABSTRACT

The study reveals the use of poly(styrene-co-divinylbenzene) as a support for Cp_2ZrCl_2/MAO catalyst for copolymerization of ethylene/1-tetradecene. It was aimed to determine the effect of ethylene per 1-tetradecene ratios on the catalytic activity and properties of the polymer. Ethylene/1-tetradecene copolymerization reactions were carried out in a 100 mL semi-batch stainless steel autoclave reactor, activated by MAO cocatalyst at 70 °C and 6 psi of ethylene pressure at various initial comonomer concentrations. From the analysis of the resulting support particles by SEM, it was found that the active species are located on the particle surface and they have uniformly distributed throughout the particles. The copolymerization has higher activity than homopolymerization. In addition, it was found that the activities increased when the molar ratio of ethylene/comonomer increased. The properties of copolymers produced were characterized by means of SEM, ^{13}C NMR and DSC. Based on ^{13}C NMR and DSC, all copolymer exhibited the similar distribution having the majority for the triad of EEE and copolymer crystallinity decreased slightly with increasing comonomer concentration.

คำสำคัญ เอทิลีน โคพอลิเมอร์ไรเซชัน, ตัวเร่งปฏิกิริยาเมทัลโลซีน, พอลิสไตรีนโคไดไวนิลเบนซีน

Keywords: Ethylene copolymerization, Metallocene catalyst, Poly(styrene-codivinylbenzene)

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INTRODUCTION

Nowadays, polymer and plastics are playing the important role on the material industry. This is because they exhibit many useful properties, such as low density, high strength, and resistance to chemical attack, as well as being cost-effective. Otherwise the demands for the plastics increase in huge quantities every year. Among synthetic polymers, polyethylene is the major polymer and the largest of production in plastic industry [1–2]. Polymers play an important role in many applications, especially linear low-density polyethylene (LLDPE). The LLDPE has many advantages such as low density, good mechanical properties, and easy fabrication and recycling. Therefore, it has been used to produce many products such as shopping bags, food packaging film, plastic pipe and house appliances, etc. [3-5]. The linear low-density polyethylene (LLDPE) can be commercially produced by copolymerization of ethylene and higher 1-olefin using metallocene catalysts [6].

As known, the homogeneous metallocene catalysts have two major disadvantages; the lack of morphology control and reactor fouling. Therefore, binding these metallocene catalysts onto inorganic supports as supported metallocene catalysts can overcome those drawbacks [7]. Numerous studies have been reported dealing with the heterogenization of single-site catalysts. They mainly consider the use of inorganic based supports such as silica, alumina or magnesium chloride [8–9]. However these supports suffer from several drawbacks, including the need for complex chemical treatments to get the appropriate particle morphology and the presence of residual inorganic fragments within the produced polyolefins that may affect their mechanical and optical properties. Nowadays, more and more attention is paid to the design and the use of organic supports. Organic supports offer significant advantages over their inorganic equivalents: they do not require fastidious preparation and pretreatment, and can be easily functionalized to accommodate the metallocene catalyst. Unlike inorganic supports, the organic residues should not significantly affect the final polyolefin properties [11].

Organic supports for metallocenes are mainly based on polystyrene (PS) because of its well defined structure, ready availability, and incorporation into the product polymer [12]. As solid beads crosslinked with divinylbenzene (DVB), however, PS is often hindered in fragmentation. It is therefore necessary for PS to be improved to meet the requirements for metallocene supports [13]. Modified poly(styrene-co-divinylbenzene) beads have been used widely as organic carriers for immobilizing metallocene catalysts. The metallocene immobilized on the crosslinked polystyrene exhibited good activity, and a polyolefin with the desired morphology was obtained. The reversibly crosslinked networks of polystyrene facilitate carrier fragmentation during polymerization [14].

OBJECTIVE

The objective of this work is to investigate effect of the ratio of ethylene/1-tetradecene on the catalytic activity of copolymerization and properties of the polymer in the poly(styrene-co-divinylbenzene) supported Cp_2ZrCl_2/MAO catalyst system.

EXPERIMENT

Materials

All operations were manipulated under an argon atmosphere using glove box and/or standard Schlenk techniques. Ethylene (polymerization grade) was obtained from the National Petrochemical Co. Ltd., Thailand. Poly(styrene-co-divinylbenzene) (PS, 2% divinylbenzene) was purchased from Aldrich Chemical Company (Thailand). Methylaluminoxane, (MAO, 10% in toluene) was donated BY PTT Research and Technology Institute (Thailand). 1-tetradecene (99%) was purchased from Aldrich Chemical Company, Inc. and purified by distilling over CaH_2 under argon atmosphere before use. Toluene was donated by the Exxon Chemical, Thailand Co. Ltd. It was dried over dehydrated $CaCl_2$ and distilled over sodium/benzophenone.

Preparation of supported MAO

Commercial poly(styrene-co-divinylbenzene) (PS beads) was heated under vacuum at 80 °C for 5 hr. After that 10 mL MAO was impregnated onto 1g of PS beads in schlenk tube by injection of 10 ml of toluene and stirred for 5 hr. Solid part was washed 5 times with toluene (10) ml and removed the toluene by drying under vacuum to obtain power of supported MAO (PS /MAO).

Polymerization procedure

The ethylene/1-tetradecene copolymerization reactions were carried out in a 100 mL semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, the desired amounts of the supported MAO and the toluene [needed to make the total volume of 30 mL] were introduced into the reactor. The desired amount of Cp_2ZrCl_2 (5×10^{-5} M) and MAO ($[Al]_{MAO}/[Zr]_{cat} = 5200$). Then, the reactor was immersed in liquid nitrogen, followed by addition of the 1-tetradecene into the frozen reactor. The reactor was heated up to the polymerization temperature at 70 °C. By feeding a fixed amount of ethylene (0.018 mole ~ 6 psi) into the reaction mixture, the ethylene consumption can be observed corresponding to the ethylene pressure drop. The reaction of polymerization was terminated by addition of acidic methanol. The time of reaction was recorded for purpose of calculating the activity. The precipitated polymer was washed with methanol and dried at room temperature.

Characterization

***Scanning electron microscopy and energy dispersive X-ray spectroscopy:* SEM and EDX** were used to determine the sample morphologies and elemental distribution throughout the sample granules, respectively. The SEM of JEOL mode JSM-5800LV was applied. EDX was performed using Link Isis series 300 program.

***Differential scanning calorimetry*: DSC** The melting temperature of ethylene/1-olefin copolymer products was determined with a Perkin–Elmer diamond DSC. The analyses were performed at the heating rate of 20°C min^{-1} in the temperature range of 50-150 °C. The heating cycle was run twice. In the first scan, sample was heated and then cooled to room temperature. In the second, sample was reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

***Nuclear magnetic resonance*: ^{13}C NMR** spectroscopy was used to determine comonomer incorporation and polymer microstructure. Comparison of the positions of peak in the ^{13}C NMR spectrum of polymer sample with characteristic leads to identification of the sequence of the comonomer incorporation. The ^{13}C NMR spectra were recorded at 110 °C using BRUKER magnet system 3000 MHz/54 mm. The copolymer solutions were prepared using 1, 2, 4-trichlorobenzene as solvent and chloroform-d for an internal lock.

RESULTS AND DISCUSSION

Characteristics of support

The morphologies and aluminium (Al) distributions of the supports after impregnation with MAO were determined using SEM and EDX, respectively. The distribution of Al can be identified using the EDX mapping as shown in Fig. 1(a1., a2.), indicating that Al element representing the active species was distributed on the surface layer and distributed uniformly throughout the PS beads. The SEM of the PS supported MAO is shown in Fig. 1(b.) showing that spherical shape for supports was mainly observed. The typical measurement curve for the quantitative analysis using EDX is shown in Fig. 2, indicating that average Al concentration on PS supports.

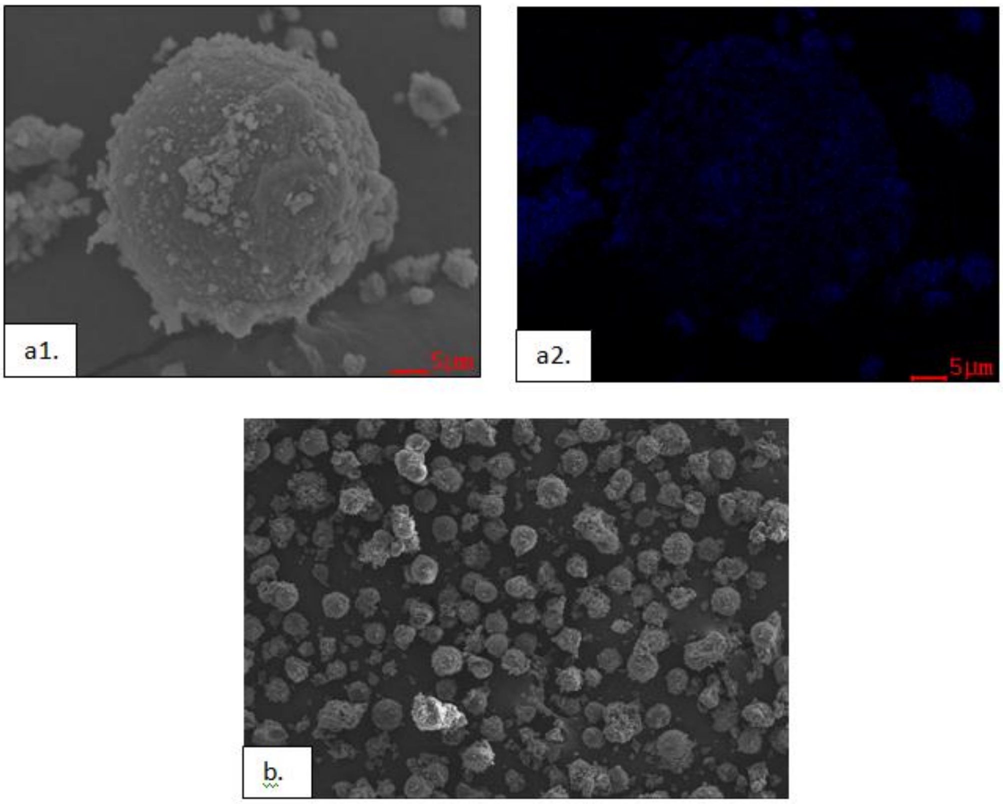

Fig 1. SEM/EDX of MAO supported onto PS: (a1., a2.) EDX mapping for Al distribution on PS, and (b.) SEM of PS supported-MAO particles

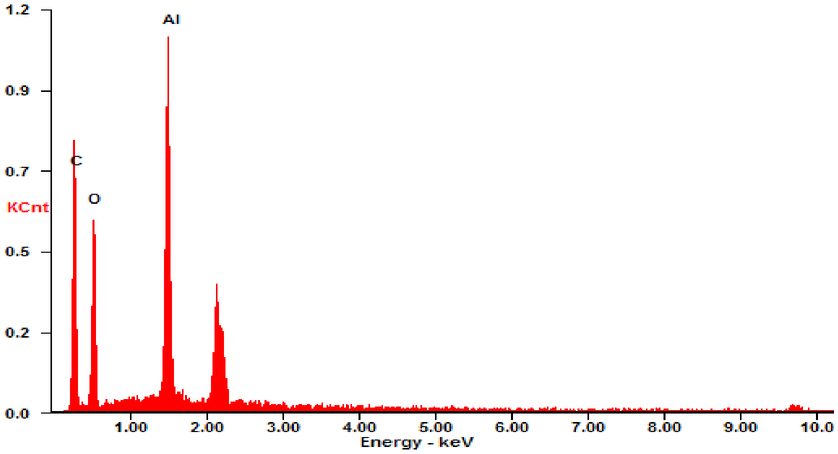

Fig 2. A typical spectrum of the supported MAO from EDX analysis used to measure the average $Al_{[MAO]}$ concentration on PS supports

Copolymerization activity

Table 1. Copolymerization activity of ethylene/1-tetradecene[a]

Run	**Mole ethylene/1-tetradecene**	**Yield (g)**	**Activity (kgPE/molZr h^{-1})**
1	no 1-tetradecene	0.67	8,729
2[b]	1:0.25	1.03	32,960
3	1:0.25	0.85	14,167
4	1:0.5	0.89	23,421
5	1:0.75	1.84	36,616

[a] Copolymerization conditions: Al/Zr = 5200, Temperature = 70 °C, 50 psi of ethylene pressure was applied.

[b] Without supports

From Table 1, it was found that ethylene/1-tetradecene copolymerization exhibits higher activity than homopolymerization (run 1).When comparing the activities between homopolymerization and copolymerization, it can be seen that the addition of the comonomer in the system yields better activity. The enhancement of activity catalyst by 1-tetradecene is called the "comonomer effect",as well as the concentration of comonomer in feed have a major influence on the catalytic activity and the presence of the comonomer increases the activity compared to that with the absence one. In addition, the activities for the ethylene/1-tetradecene copolymerization by heterogeneous systems (no support) were lower than those using homogeneous systems. A possible reason for this observation is that mass transfer in the heterogeneous systems depressed the activity catalyst and the deactivation of cocatalyst due to immobilization of the MAO onto supports.

Characteristics of polymer

The obtained copolymers were further characterized using SEM, ^{13}C NMR, and DSC measurements. The typical SEM micrographs of copolymers are shown in Fig. 3 indicating the morphologies of ethylene/1-tetradecene copolymer obtained from the different concentration of comonomer. It is suggested that the use of higher concentration of comonomer seemed to increase the degree of agglomerate.

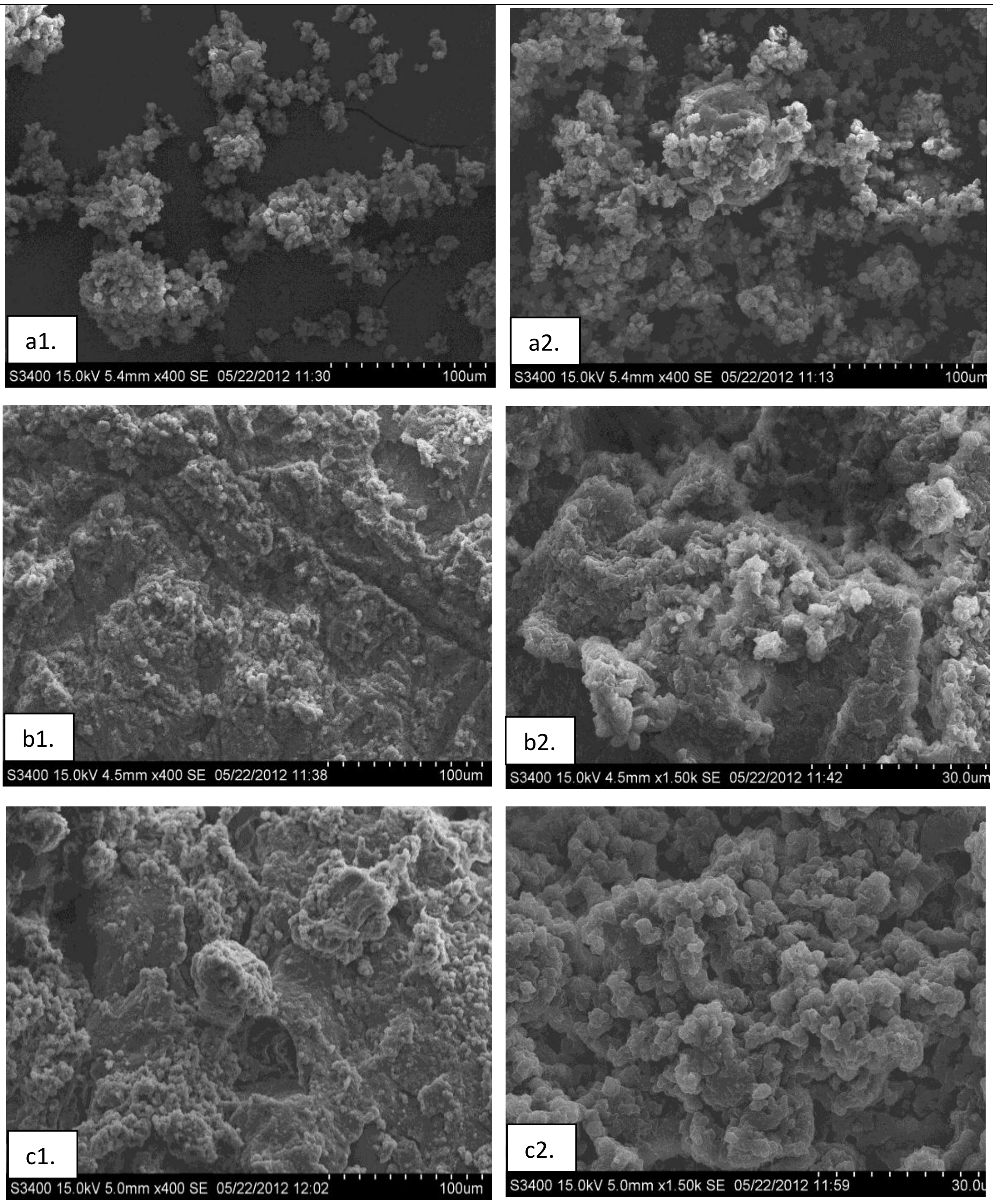

Fig 3. SEM micrographs of copolymers obtained from different ratio of ethylene/1-tetradecene; (a.) 1:0.25, (b.) 1:0.50, (c.) 1:0.75.

The quantitative analysis of triad distribution for all copolymers was conducted on the basis assignment of the^{13}C NMR spectra. The triad distribution for all copolymers is shown in Table 2. As can be seen, all copolymers exhibited the similar distribution having the majority for the triad of EEE. Considering comonomer insertion it was observed that the use higher concentration of comonomer apparently yielded the increased degree of insertion. The DSC results as shown in Table 2, it indicates that, the homogeneous catalyst produced polymer with high melting temperature (T_m) ~139 °C and T_m of copolymer tended to decrease with the use of PS as a support. This behavior was attributed to the increased degree of 1-olefin insertion, which was in agreement with ^{13}C NMR results. (The crystallinity of copolymers can be decreased with a higher degree of 1-tetradecene insertion.)

Table 2. Triad distribution[a] and properties of resulting ethylene/1-tetradecene copolymers.

Run	**Ethylene/1-tetradecene**	**Triad distribution**						**T_m (°C)**
		[EEE]	**[TEE]**	**[ETE]**	**[TET]**	**[ETT]**	**[TTT]**	
2[b]	1:0.25	0.826	0.067	0.063	0.030	0.000	0.014	119
3	1:0.25	0.882	0.057	0.042	0.013	0.000	0.006	116
4	1:0.50	0.873	0.062	0.040	0.006	0.006	0.013	110
5	1:0.75	0.630	0.041	0.123	0.102	0.000	0.104	n.o.[c]

[a] Triad distribution use to describe comonomer incorporation in polymer chain ; E refers to ethylene and T refers to 1-tetradecene.

[b] without supports

[c] not observed

CONCLUSIONS

In this article, we have reported the synthesis of polyethylene from copolymerization of ethylene/1-tetradecene via poly(styrene-co-divinylbenzene)-supported Cp_2ZrCl_2/MAO catalyst by varying ratio of ethylene/1-tetradecene. The results show that copolymerization has higher activity than homopolymerization. The increase of initial comonomer concentration caused an increase in catalytic activity. Copolymers exhibited the similar distribution having the majority for the triad of EEE that measured by ^{13}C NMR. DSC results revealed that the homogeneous catalyst produced polymer with melting temperature higher than heterogeneous catalyst and melting temperature of copolymer tended to decrease with the use of PS as a support.

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