

CHAPTER II

LITERATURE REVIEWS

This chapter presents the literature reviews of the previous works related to this research. Both copolymer synthesis part and polymer blend part are shown as below.

2.1 Copolymer synthesis.

Coates *et al.* [11] also reported the synthesis of a poly(syndiotactic propylene-*block*-(ethylene-*r*-propylene)) with a metallocene catalyst system. The products were highly syndiospecific and the process considered to be living polymerization. Catalytic living polymerization proceeds without appreciable chain termination or transfer, thus high molecular weight polymers were obtained. The reaction can proceed even after halt on the order of days. The living nature of the catalyst allows the synthesis of block copolymers previously unavailable from Ziegler-Natta catalysts.

Y. Fukui and M. Murata [12] also reported the synthesis of poly(propylene-*block*-(ethylene-*co*-propylene)) by living polymerizations. The reactions were performed with various metallocene catalyst systems at low temperatures. With the above metallocene catalyst systems, Poly (atactic propylene-*b*-(ethylene-*co*-propylene)) (Poly(ataP-*b*-EP)) block copolymers can be prepared by the addition of ethylene monomer during the living polymerization of propylene at low temperature. The M_n (molecular weight of polymer) of the resultant copolymer showed a higher value than that of corresponding homopolypropylene while retaining the narrow molecular weight distribution. By the transmission electron microscopy (TEM) analysis, a microphase-separated morphology with ca. 50–100 nm dimension was observed in an iso-PP blended with Poly(ataP-*block*-EP).

H. Mori *et al.* [13] were developed high-pressure-type stopped-flow polymerization system for synthesized a poly(propylene-*block*-(ethylene-propylene)), having a variable molecular weight, by using Ziegler-Natta catalyst. The preliminary homopolymerization experiments of propylene at 1-6 atm for 0.1 s with an MgCl₂-supported Ziegler catalyst and TEA indicated that the polymer yield and molecular weight of the resulting polypropylene were proportional to the monomer concentration in the system. This indicates that the catalyst activity is constant and the unfavorable side reactions can be negligible, i.e., independent of the monomer pressure. The higher propylene and ethylene concentrations, which could be regulated by the increase of pressures of the vessels in the apparatus, were found to induce a higher molecular weight of the resulting block copolymer without a significant change in the molecular weight distribution and microstructure. The CFC (Cross Fractionation Chromatography), DSC, and AFM analyses results indicated that the increased molecular weight had an influence only on the lamellar thickness but had no effect on the crystallinity and its distribution of the block copolymer.

Mikio Yamahiro *et al.* [14] investigated the influence of electron donors on the synthesis of poly(propylene -*block*- (ethylene-co-propylene)) (Poly(P-b-(E-co-P))) using a modified stopped-flow polymerization method. The product was examined in terms of correlation of the microstructures of the polymer with its crystalline morphology. The results of propylene homopolymerization and ethylene-propylene copolymerization indicated that the application of suitable internal and external donors induced an improvement in the stereoregularity of polypropylene (PP) without a decrease in the initial activity and a significant change in the monomer composition and monomer sequence distribution of poly (ethylene-co-propylene) (PE-co-PP). The TiCl₄/ethylbenzoate/MgCl₂ – cyclohexylmethyldimethoxysilane catalyst system was found to produce Poly(P-b-(E-co-P)) having highly isotactic PP segments. The resulting block copolymers were investigated by CFC (cross-fractionation chromatography) and differential scanning calorimetry, suggesting that the improved stereoregularity of the PP part in the Poly(P-b-(E-co-P)) had an effect only on the

crystallinity and crystallinity distribution but had no influence on the crystallizability and lamellar thickness of the block copolymer.

Yong-Woo Shin *et al.* [15] synthesized ethylene-propylene random copolymers, Poly(E-r-P), with isotactic sequence of propylene in the copolymer by using a MgCl_2 -supported $\text{Cr}(\text{acac})_3$ catalyst and controlled propylene content by the monomer concentration (in other word, vary pressure of P or E). By vary the pressure of P and E, the isotactic PP portion can be obtained. However, Ethylene-rich copolymers exhibit the orthorhombic form of PE and propylene-rich copolymers exhibit the monoclinic form of PP.

G. H. Zohuri *et al.* [16] synthesized ethylene-propylene copolymers (Poly(E-r-P)) by using high-activity Ziegler–Natta catalyst of TiCl_4 -supported MgCl_2 (ethoxide type) and using ethyl benzoate (EB) and polydimethylsiloxane (PDMS) as internal donors, while *p*-methyl toluate (MPT) and triethylaluminum (TEA) were used as the external donor and cocatalyst respectively. The effects of the TEA concentration, H_2 concentration, temperature, and pressure of P/E on the yield of the polymer obtained and the glass transition temperature (T_g) were investigated by using DSC, DMTA and FTIR. It was found that, the optimum temperature of copolymerization depend on the T_g and percentage of ethylene content. Increasing the temperature of copolymerization decrease the catalyst activity and increase the ethylene content of copolymer and decrease the T_g value, to be close to the T_g of polyethylene.

Ed Kolodka *et al.* [17] synthesized novel Poly(polypropylene-graft-poly(ethylene-co-propylene)) copolymers, Poly(PP-g-EP). Firstly, synthesize isotactic poly (propylene) (PP) backbones and secondly, ethylene/propylene rubber (EPR) branches were synthesized. After that, the copolymers were investigated the thermomechanical properties of these samples by using a dynamic mechanical analyzer. Two-phase systems of EPR domains dispersed in a PP matrix were developed at above the critical EPR molecular weight (approximately 6000). This EP

domain formation gave an enhanced loss modulus compared to a commercial high impact PP product at below 40°C.

2.2 Polymer blend

K. Nitta *et al.* [18] investigated additive effects of a diblock copolymer of poly(propylene-*block*-(ethylene-*co*-propylene)), Poly(P-*b*-EP) (50–50%weight) in matrix of isotactic PP and EPR. The diblock was synthesized by short-period polymerization method by Ziegler-Natta catalyst systems. The morphology and mechanical properties of the blends of copolymer were investigated. From an electron microscopy, the block copolymer is compatible with the PP phase but incompatible with the EPR phase. Dynamic mechanical spectra showed that the Poly(P-*b*-EP) block copolymers are incorporated into the PP phase, and consequently, the EPR portions of the block are trapped into the interlamellae of PP.

Zhi-qiang Fan *et al.* [19] synthesized poly(propylene-*co*-(ethylene-*co*-propylene)), poly(iP-*co*-EP) in-situ blend by spherical Ziegler-Natta catalyst in two stages. The first stage use liquid phase propylene homopolymerization and the second stage use gas phase ethylene-propylene copolymerization. The copolymer was fractionated by temperature-gradient extraction fractionation. The fractions were characterized using FTIR, ¹³C NMR, DSC and WAXD. Mainly three portions were attained from TREF that are the pure ethylene-propylene random copolymer, pure Polypropylene, and different length of copolymer of EP with PE or PP segments. The impact strengths of synthesized polymers were measured, and the results showed that increasing the portion of the copolymer has a positive effect on the impact strength. The impact properties both at room temperature and low temperature were enhanced with the existing of copolymer fraction.

Koh-Hei Nitta *et al.* [20] studied the morphology and mechanical properties of novel block copolymers consisting of Poly(isotactic propylene -*b*- (ethylene -*r*-propylene), Poly(iP-*b*-EP) synthesized by a short-period polymerization method by

using DSC, AFM(atomic force microscopy), DMA, and a rheo-optical technique. It was found that the novel block copolymers show a single glass transition. EPR segments of the copolymer are trapped into the amorphous region of segments of PP. Furthermore, the rheo-optical analysis demonstrates that a drawing process of the block copolymer (EPR-rich) induced orientation of the segments of PP lamellae in the segments of EPR matrix.

Koh-Hei Nitta *et al.* [21] investigated the additive effects of the novel synthesized ethylene-propylene random (EP) copolymers in the blend with homopolymer isotactic polypropylene. The properties of the morphology and mechanical properties of isotactic polypropylene (iPP) blends were investigated by using polarized optical microscopy, transmission electron microscopy, dynamic mechanical analysis and tensile behavior. It was found that, the EP copolymers with portion of propylene-unit content of more than 84 mol% were miscible when blended with iPP. Whereas the EP copolymers with propylene content of below 77 mol% are immiscible. The crystallizable PP sequences in these EP copolymers were incorporated into crystal lattice of the homopolymer iPP and the other portions in the EP chains were excluded to the amorphous phases. The iPP/EP blends showed the phase-separated morphology.

However, all these mentioned methods are not appropriate to perform in the industrial applications. To overcome these problems, this work represents the new simple method for synthesis of polypropylene-*co*-poly(ethylene-propylene) (PP-*co*-EP) copolymer by using Ziegler-Natta catalyst which might apply to use in the industrial production. This polymer structures which synthesized by simple method can adhere in polypropylene matrix as same as the copolymer from these complicated methods.