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THESIS

**MICROSTRUCTURES AND FUNCTIONALIZATION OF
METALLOCENE-CATALYZED POLYOLEFINS**



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Chapter 1

General introduction

- Historical aspects of polyolefins -

1. Polyolefins

Polyolefins, represented by polyethylene (PE) and polypropylene (PP), are indispensable materials as synthetic polymers having huge social impact. They are used in our daily lives in such applications as films, pipes, automobile parts, electric and electronic parts, medical and sanitary products, toys, construction materials, and agricultural materials.

In general, synthetic polymers have been dramatically changed our daily lives, and provided humankind with huge benefits. Historically, since the first synthetic polymer (i.e. phenol resin) was discovered in 1907 by Bakeland, a number of synthetic polymers that include urea resin, melamine resin, epoxy resin, polyamide, polyester, poly(vinyl chloride), polystyrene, polyethylene and polypropylene have been developed [1]. Needless to say, they are light, rustless and capable of being mass-produced due to their excellent processability compared with conventional materials such as metal, wood, glass, paper and ceramic. In addition, a diversity of polymer frameworks, in combination with polymer alloys and compound technologies, provides a wide range of characteristic properties. These well-balanced features are distinguishable from those of conventional materials. Therefore, synthetic polymers have replaced these common materials in according with intended uses.

Among synthetic polymers, polyolefins are the most widely used classes of industrial plastics in these days. Total amounts of polyolefins produced worldwide every year are almost one billion tons, accounting for 50 % of the total amounts of synthetic polymers (figure 1-1) [2]. Those polymers possess many useful properties, namely, lightness, mechanical strength, toughness, good stability for chemicals and excellent processability (injection molding, extrusion molding, etc), and so on. Those features as

well as polyolefin's cost-effectiveness make them suitable for commodity applications which include packaging films, containers, bottles, grocery sack, agricultural materials, household electric appliance, automobile parts, and so on. In addition, polyolefins are clean materials because they are composed of only carbon and hydrogen atoms. Also, they are easily recycled. These advantages lead to a reduction of environmental burdens.

Total amounts of synthetic polymers produced worldwide in 2003

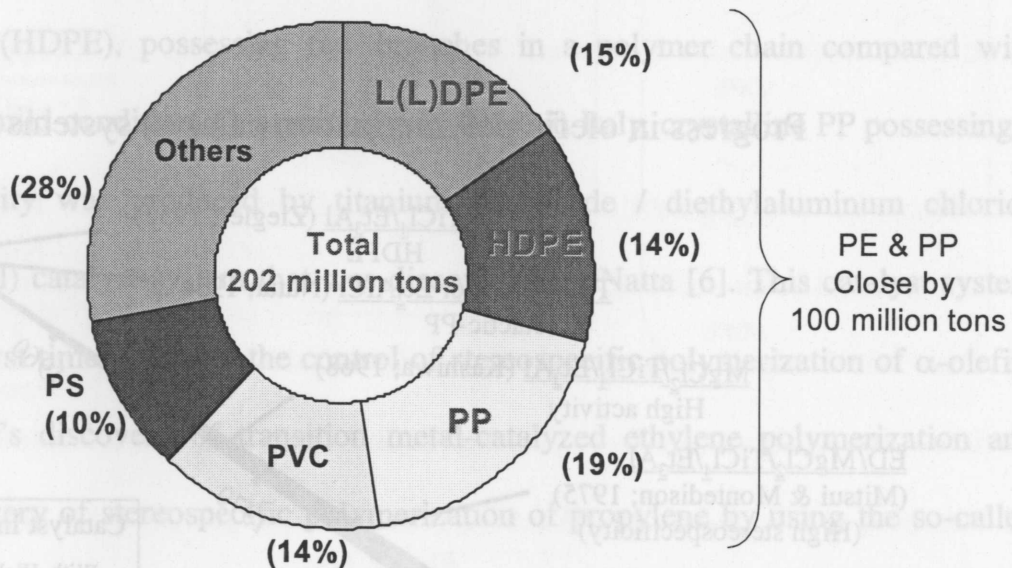


Figure 1-1

On the basis of global demand, the growth rate of these polyolefins is predicted to rise up to 5 % annually by the year 2010, because polyolefins are finding their way into the market to replace common materials such as metal and ceramic [3].

2. Development of polyolefins as commodity materials

In early stage of polyolefin industry, low density polyethylene (LDPE) was produced

by the radical process using organic peroxide initiators at high temperature (200-300 °C) and pressure (1000-3000 atm) [4]. LDPE is an ethylene homo-polymer with many branches and possesses good processability, clearness and softness due to the presence of many branches. The control of their strength, however, is difficult because the branches possess various chain lengths. In addition, the harsh polymerization conditions of LDPE production demand a considerable capital investment and need a huge energy to produce the material. Therefore, the amount of production of LDPE has not changed since those days.

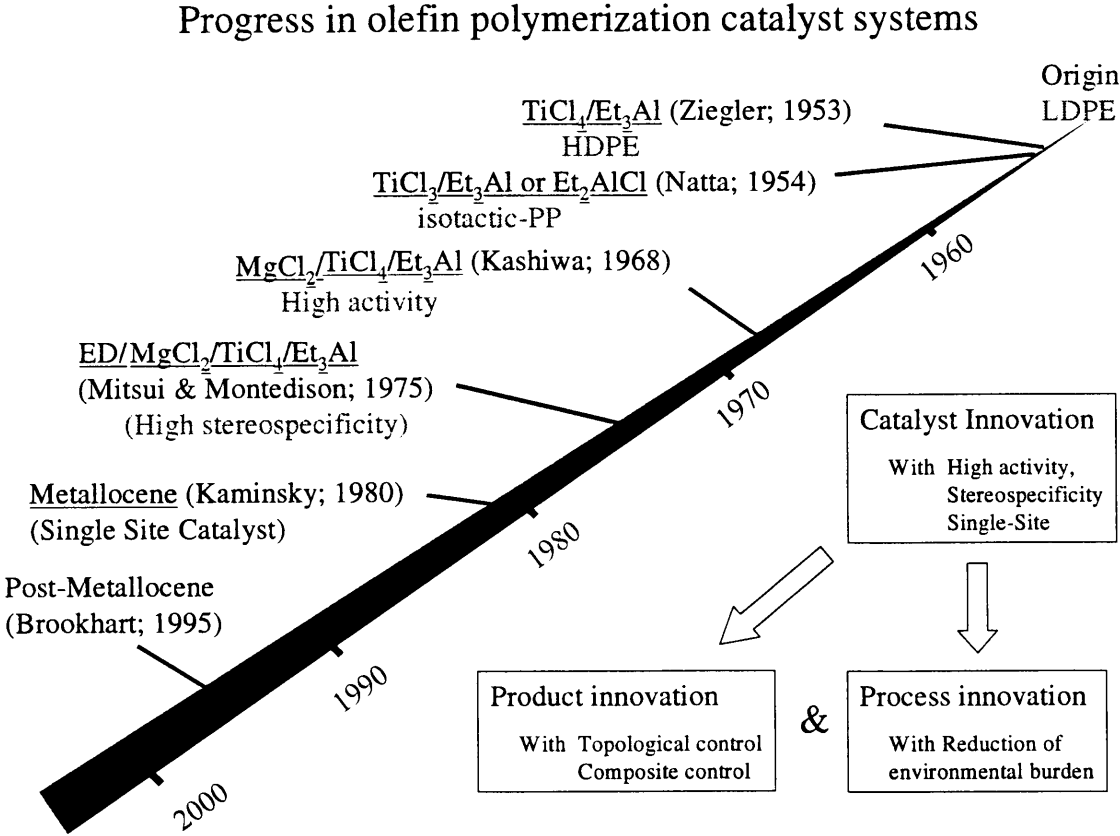


Figure 1-2

The glory of polyolefins in these days has been brought with developing their properties such as ones mentioned above. It is regarded that one of the most important

factors for their success has been catalyst system. The development of catalyst systems for olefin polymerizations has brought the product innovation in polyolefin industry (figure 1-2).

2.1. Polyolefins produced by Ziegler-Natta catalyst systems

In 1953, one of the most important discoveries was done by Ziegler in Germany. His discovery, the titanium tetrachloride / triethylaluminum ($\text{TiCl}_4/\text{Et}_3\text{Al}$) catalyst system for a coordination polymerization of ethylene [5], has an ability to produce high density polyethylene (HDPE), possessing few branches in a polymer chain compared with LDPE under mild condition. Continuously, in 1954, in Italy, crystalline PP possessing a high isotacticity was produced by titanium trichloride / diethylaluminum chloride ($\text{TiCl}_3/\text{Et}_2\text{AlCl}$) catalyst system that was discovered by Natta [6]. This catalyst system was for the first time to enable the control of stereospecific polymerization of α -olefin. Thus, Ziegler's discovery of transition metal-catalyzed ethylene polymerization and Natta's discovery of stereospecific polymerization of propylene by using the so-called Ziegler-Natta catalyst lead the evolution of a new generation of catalysts and polyolefin materials.

After the discovery of those Ziegler-Natta catalyst systems, many scientists and engineers have emphasized to discover a high performance catalyst systems, for example, MgCl_2 -supported TiCl_4 catalyst system [7, 8], which showed good performance in an activity, an ability of incorporation of comonomers, stereo-selectivity, and so on. As the results, polyolefin materials have used not only for dairy goods (toys, packages, containers, and so on) but also replacing goods of engineering plastics. Moreover, many kinds of polyolefins such as linear low density polyethylene (LLDPE),

2.2. Polyolefins produced by metallocene catalyst systems

After the discovery of Ziegler-Natta catalyst in early 1950's, indeed, several catalyst systems regarded as single-site catalyst have been reported. For examples, vanadium-based catalyst developed by Natta [9]. However, the serendipitous discovery of the activating effect of a small amount of water on the system of dicyclopentadienyl zirconiumdimethyl / trimethylaluminum ($\text{Cp}_2\text{ZrMe}_2/\text{AlMe}_3$) and the subsequent development of the controlled synthesis of methylaluminoxane (MAO) by Kaminsky and Sinn in 1980 were major breakthroughs in olefin polymerization catalyst system as single-site catalyst [10]. The catalytic activity of the metallocene catalyst is 10 times larger than that of the MgCl_2 -supported TiCl_4 catalyst.

An important aspect in metallocene catalysts, differing from heterogeneous Ziegler-Natta catalysts, is the narrow molecular weight distribution of homogeneously produced polymers. While polyolefins obtained with typical Ziegler-Natta catalysts have broad molecular weight distributions ($M_w/M_n = 5-10$), metallocene catalysts produce polymers with M_w/M_n approximately 2. An M_w/M_n value of 2 is predicted by Schulz-Flory statistics for polymers arising from identical catalyst centers with fixed rates of chain propagation and chain termination. A molecular weight distribution (MWD) of 2 is thus regarded as evidence that only a single catalyst species contributes to polymer formation in a homogeneous catalyst system (therefore metallocene catalysts are called "single site catalysts"), which makes the properties of the resulting polyolefins predictable upon determining the structure of the catalyst.

Another aspect of metallocene catalysts, in general, is that an introduction of bulky monomer into the center of active point of catalyst is easy. The homogeneity of metallocene catalysts leads to the formation of polymers with uniform incorporation of

α -olefin comonomers, because the electronic and steric properties of all of the catalytic sites are approximately the same. LLDPE, isotactic-PP (i-PP), syndiotactic-PP (s-PP) and EL have been produced by metallocene catalysts with better properties compared with ones of former polymers.

And, one of the most attractive points of metallocene catalyst systems is to enable to design the structure of catalyst in molecular size and to synthesize them by organic (or organometallic) synthesis techniques. Therefore, it's possible that the catalyst is designed to elucidate a relationship between catalyst structure and catalytic performance that includes precise control over resulting polymer microstructure (figure 1-4) [11, 17-27].

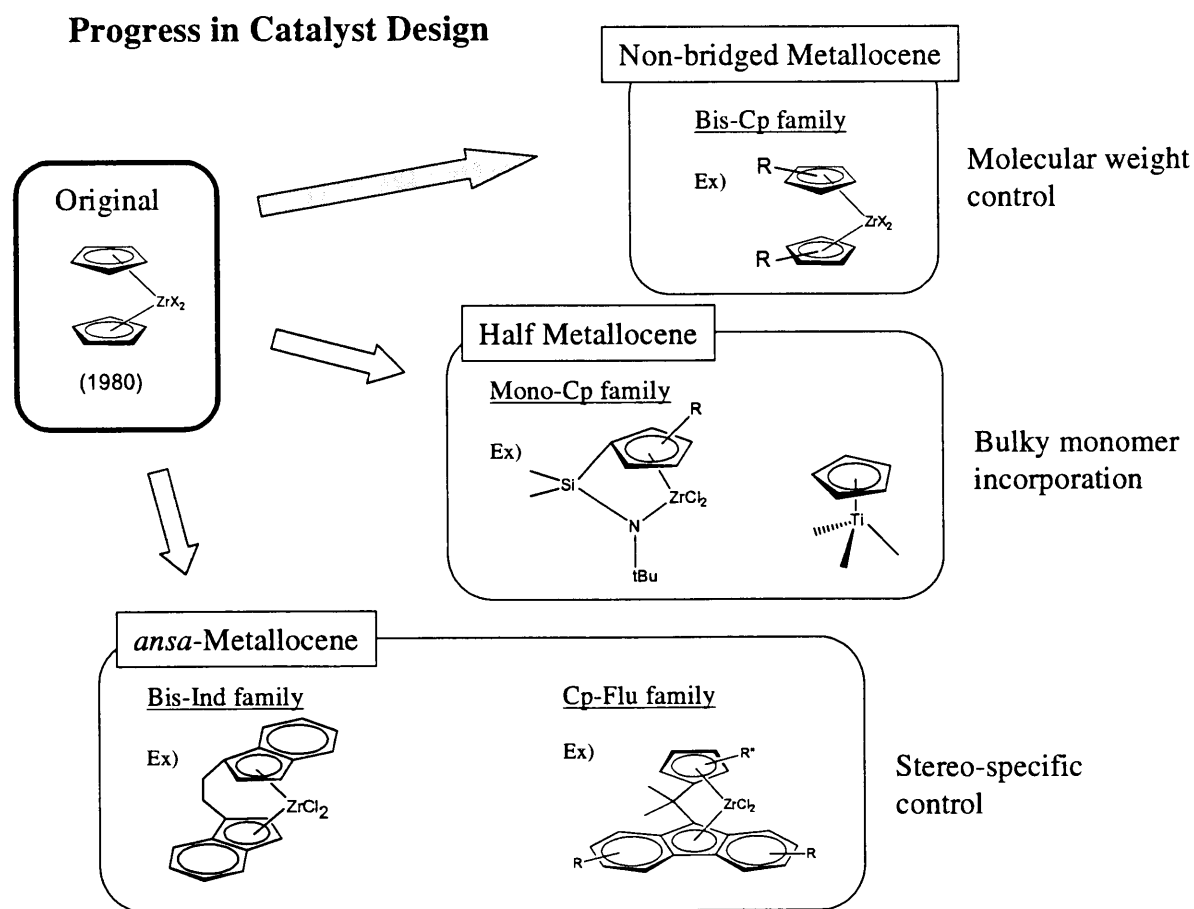


Figure 1-4

Those let the field of olefin polymerization catalysts from engineering technology to science. In addition, the analysis of the structures of polymers produced by metallocene (or single site catalysts) has made it possible to investigate the polymerization reaction of olefins more precisely.

After the discovery of metallocene catalyst systems, many scientists have studied on creation of a next polymerization catalyst system, so-called post-metallocene [12-16]. Several catalyst systems of them show good abilities in olefin polymerization, namely, living nature, very high molecular weights of resulting polymers, and so on [28-33]. Therefore, post-metallocene catalyst system would be considered next classes of catalyst to produce functional polyolefins.

3. Development of polyolefins for new materials

In order to improve the properties of polyolefin materials further, what are important are the precise control of polymer chain structures and the investment of functionalization in polymer chain [34] (figure 1-5).

3.1. High performance polyolefins with composition and topology control

So far, polyolefins have been used in architectural material fields as like automobile parts, households, seal materials, processability, and so on, mainly. Therefore, it's important of polyolefins to improve properties of mechanical strength and heat-resistance for application in these fields. To this end, the precisely control of architectures of polymers including composition and topologies is to be important (figure 1-6).

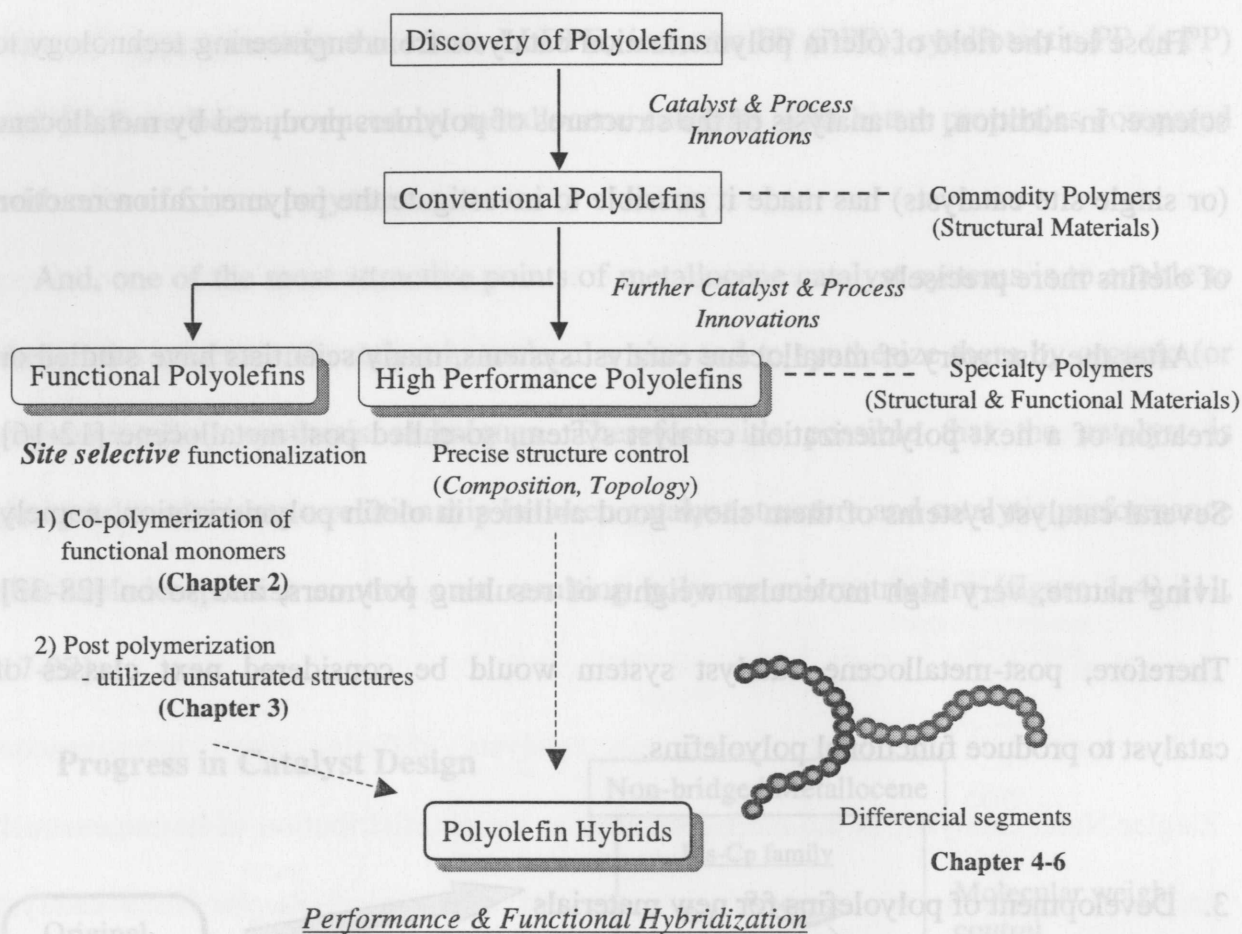


Figure 1-5

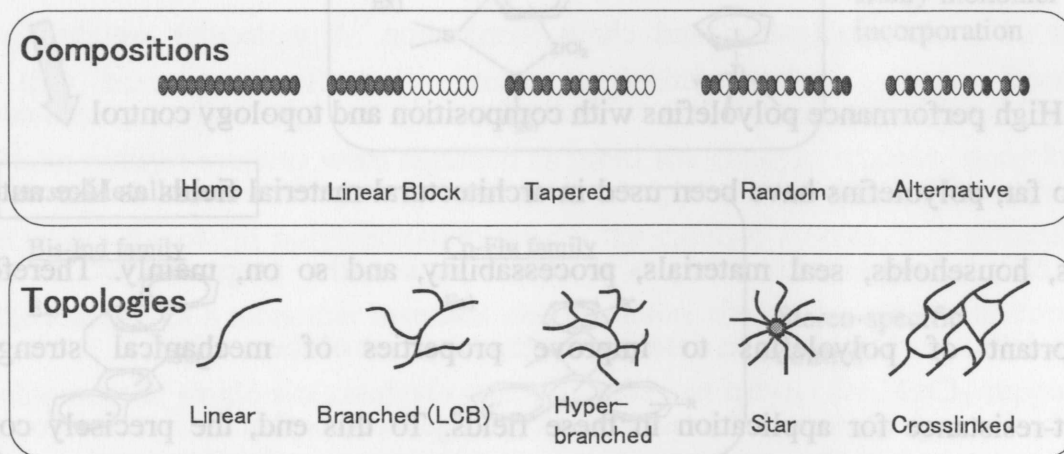


Figure 1-6

The control of compositions of polymers is expected to be effective to control the softness, heat-resistance, and so on. For example, it was reported that PE-*block*-poly(ethylene-co-propylene) and s-PP-*block*-poly(ethylene-co-propylene) was synthesized by post metallocene catalyst systems [35]. Concerning tapered polymer, it was reported as effective optical materials [36]. It was also reported that the control of topologies is effective to enhance a processability and mechanical strength [37, 38]. Ethylene based long-chain branched copolymer produced by metallocene catalyst system showed the excellent property balance between the processability and toughness. Also long chain branched PP indicated the excellent balance of melt elasticity and mechanical properties. Network polymers, so-called cross-linked polymers, possess the good elasticity [39]. Those polymers were used as abrasion-resistance materials such as a tire rubber or tubes for automobile.

3.2. Functional polyolefins

Despite the great success of polyolefins, deficiencies such as lack of reactive functional groups in the polymer structures have limited some of their end uses, particularly those in which adhesion, dyeability, paintability, printability or compatibility with other functional polymers is paramount. Therefore, many research activities were geared toward the preparation of functional polyolefins. And, many scientists have studied to overcome this disadvantage by introducing suitable functional groups in polyolefins to broaden the applications of polyolefins to highly profitable fields [40]. Theoretically, there are two possible approaches to the synthesis of functional polyolefins, namely, a) direct copolymerization of olefins with functional

monomers by using polymerization and catalyst technologies, and b) post polymerization reaction with polyolefins. In those cases, also, the precise control of polymer architectures, that is, site control of introduction of functional moieties into the polymer chain, would be important. So, in this sense, the study on structures of polyolefins and the investigation of each reaction in polymerization, that is insertion of monomer, termination of propagation of polymer chain, is helpful to design and to control the macromolecule architectures (figure 1-7).

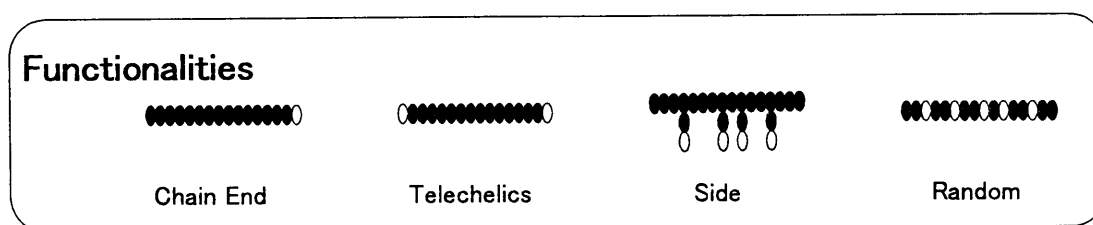


Figure 1-7

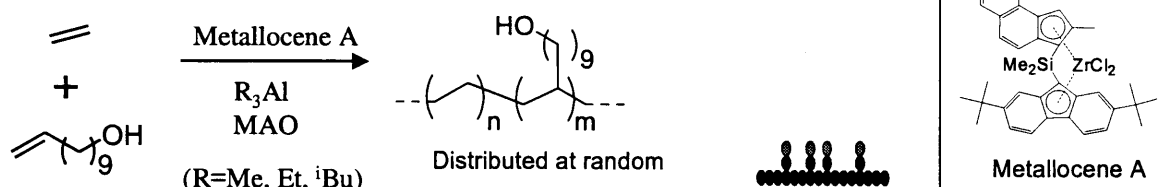
3.2.1. Copolymerization of olefins with functional monomers

The direct method for synthesis of functionalized polyolefins involves the copolymerization of an olefin with comonomers having the desired functional groups. A large number of studies of copolymerization of olefins by metallocene catalysts have been reported with functional monomers such as ω -chloro- α -olefins [41], 5-(N,N-diimidopropylamino)-1-pentene [42], cubic silsequioxane [43], 6-tert-butyl-2-(1,1-dimethylhept-6-enyl)-4-methyl phenol [44], hindered amine light stabilizers (HALS) [45], carbazole-based comonomer [46], Oxazoline-based comonomer [47], allylanisole [48], and so on.

Among them, the comonomers having the hydroxyl groups have been used for copolymerization of olefins in many cases. Those hydroxyl groups of monomers are

usually protected from poisoning catalyst by chemicals such as alkylaluminum compounds. Aaltonen and his co-workers investigated to synthesize hydroxyl group containing polyolefins using metallocene catalyst systems [49]. They achieved to synthesize hydroxylated PE and PP with several kinds of metallocene. Imuta et al. have successively achieved to synthesize the terminally hydroxylated PE by using C_1 symmetrical metallocene catalyst system. They suggested that alkylaluminum compounds protecting polar moiety had influence on site selectivity for hydroxyl group in PE (figure 1-8) [50]. Hagihara and Imuta have reported the synthesis of amino terminated polyolefins using metallocene catalyst systems [51].

1. Ethylene / 10-Undecenol Copolymerization



2. Ethylene / Allyl Alcohol Copolymerization

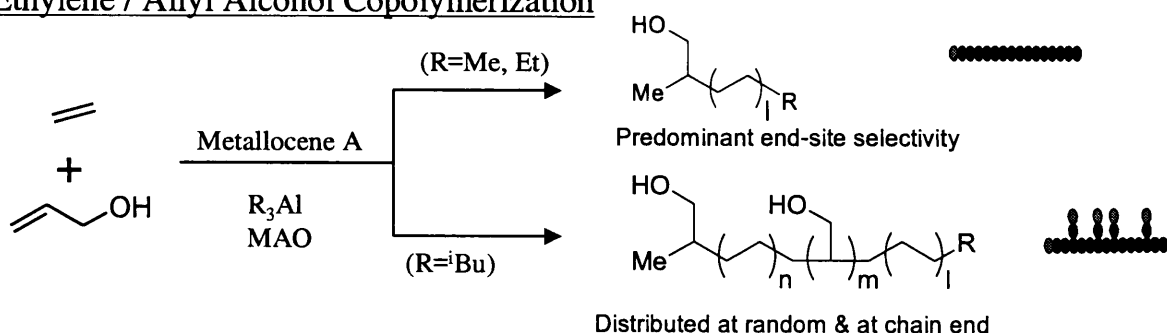


Figure 1-8

In those cases, namely copolymerization of olefins with functional monomers, metallocene catalyst systems have an advantage to synthesis functional polymers due to

their ability for polymerization of bulky monomer. However, this method is limited by the ability of many functional groups to coordinate with the catalyst/cocatalyst components, thus, causing catalyst deactivation, more or less. Furthermore, those polymerization reactions have been studied only by analysis of the chain structures of the resulting copolymers, and, the mechanism of the insertion reaction of polar monomers into the metallocene active center has never been clarified.

3.2.2. Post polymerization reaction

3.2.2.1. Direct modification of polyolefins

There are several ways to create functional polymers based on polyolefins. It's a common method that polyolefins are treated with radical initiator and functional chemicals such as maleic anhydride, halogen, (meth)acrylate monomer, and so on. Chemical modification of the pre-formed polyolefins has been usually carried out in situ during the fabrication process to reduce the production cost. In addition, surface modification of polymer materials continues to be an important area because of the many cases where the surface properties of polymers affect their utilities. For example, PE was modified with maleic anhydride through a radical reaction to improve its adhesion, and so on [52]. The oxidation of the surface of PE film and its application has been studied with chromic acid solution [53]. Plasma treatment enables to modify the surface of polymer films, effectively [54].

However, there are no facile reaction sites in saturated polyolefins. The only way is to activate the polymer by breaking some stable C-H bonds and forming free radicals along the polymer chain, as mentioned above. Those functionalization reactions are usually accompanied with many undesirable side reactions such as crosslinking and

degradation. Therefore, the current commercial processes are far from ideal ones.

3.2.2.2. Modification at unsaturated groups in polyolefins

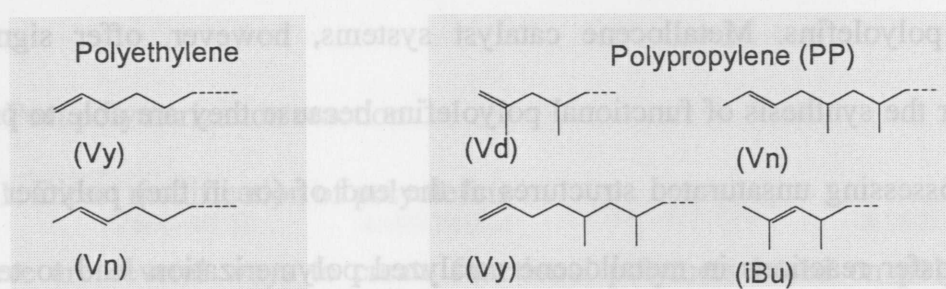
Unsaturated groups of polyolefins were able to be converted several functional groups such as epoxy group, silyl group, hydroxyl group, maleic anhydride group, and so on [55]. Unsaturated structures such as vinyl and vinylidene are generally observed in pyrolyzed polyolefins. Metallocene catalyst systems, however, offer significant advantages for the synthesis of functional polyolefins because they are able to produce polyolefins possessing unsaturated structures at the end of (or in the) polymer chain. The chain transfer reactions in metallocene catalyzed polymerization lead to terminal double bonds that are used to further chemical reactions (figure 1-9).

Halogenation [56] and amination [57] of terminally unsaturated groups of PP were described in previous papers. Oxazoline terminated PP [58] and methacrylate terminated PP [59] were synthesized from metallocene catalyzed PP having terminally vinylidene group. Terminally unsaturated polyolefins, possessing vinyl or vinylidene groups, are variable as macromonomer for cationic, radical and coordination polymerization reaction [60]. In this point, it's important to investigate unsaturated structures in polyolefins.

In case of PE, terminally vinyl and vinylene structures were produced by termination reaction of metallocene-catalyzed polymerization reaction [61]. In case of PP, β -hydrogen transfer was proposed with three pathways, namely β -hydrogen transfers to metal [62], or to monomer [63], or after secondary monomer insertion [64], to produce the vinylidene chain end structure. β -Methyl transfer is a newly discovered chain transfer mechanism in the propylene polymerization to form terminally vinyl structure

[65]. Other unsaturated structures, for instance, vinylene structure, etc., were reported in previous papers in metallocene-catalyzed polymerization of olefins [66]. Those studies are useful not only to develop functional polyolefins but also to investigate the mechanism of polymerization reactions of olefins.

Several unsaturated structures in metallocene-catalyzed polymers



Conversion of unsaturated group to functional group

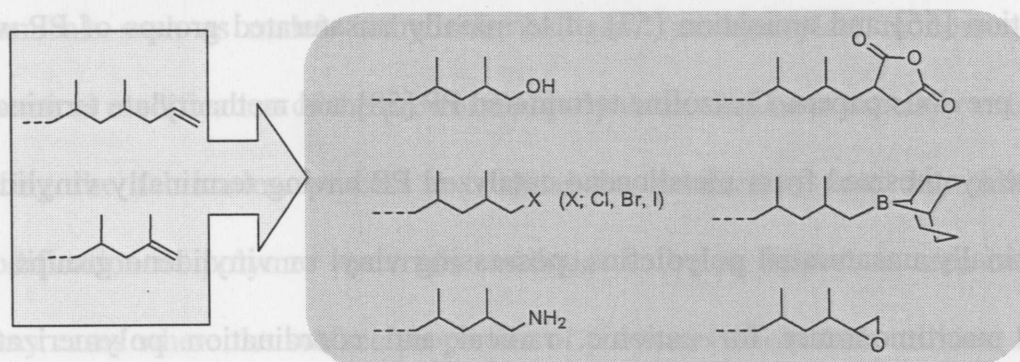


Figure 1-9

However, in those studies, several metallocenes have been used, and the assignment of ¹H NMR peaks of those unsaturated structures were actually difficult and complicated due to the peak overlapping with terminal vinylidene structure. Therefore, there is room for further investigation in those research fields.

3.3. Polymer hybrids based on polyolefins

Recent advances in polyolefin chemistry have led to the creation of polymer hybrid linking between polyolefins and polar polymer segments by combination between functionalized polyolefins, which were mentioned above, and several processes such as radical, anionic, cationic polymerizations and post polymerization reactions, bringing the ordinary polyolefins some improved and unique properties to broaden their applications. Those new polymer hybrids could be synthesized by using functionalized polyolefins as three kinds of effective tools, which are polyolefin (PO) macromonomer, PO macroinitiator and reactive PO (figure 1-10).

PO macroinitiators, which have initiation sites for radical or anionic polymerization on their backbones, can give various copolymers of the combination of PO and non-PO as block type and graft type. The borane-functionalized PO was used in combination with living anionic polymerization of ϵ -caprolactone to synthesize PP-*graft*-poly(ϵ -caprolactone) (PCL) copolymer [67]. Al-terminated PE produced by chain transfer reaction in metallocene-catalyzed polymerization could be used as a PO macroinitiator for an anionic polymerization to synthesize PE-*block*-PCL [68]. Recent development of a controlled radical polymerization has extended the possibility of synthesizing a variety of block and graft copolymer [69]. Application of that technique for polyolefins realized the creation of the well-defined polymer hybrids. Stehling synthesized PP-*graft*-polystyrene (PS) by using alkoxy-amine functionalized PP as macroinitiator of styrene that was produced by metallocene-catalyzed copolymerization [70]. Hydroxylated polyolefins were converted to PO macroinitiators, and they were used to synthesize polymer hybrid, namely PE-*block*-poly(methylmethacrylate) (PMMA) [71], PE-*graft*-poly(n-butylacrylate) (P(nBA)) [72]. Those polyolefins

mentioned above are also used for living anionic polymerization as macroinitiator to produce PE-graft-poly(propyleneglycol) (PPG), PE-graft-PCL [73]. Terminally unsaturated POs are also quite useful to synthesize polymer hybrid by conversion of their chain end to initiation sites. For examples, PE-block-PMMA, PE-block-PS and PP-block-P(nBA) were prepared from terminally unsaturated polyolefins by ATRP (figure 1-9) [74].

New Polyolefin Hybrids

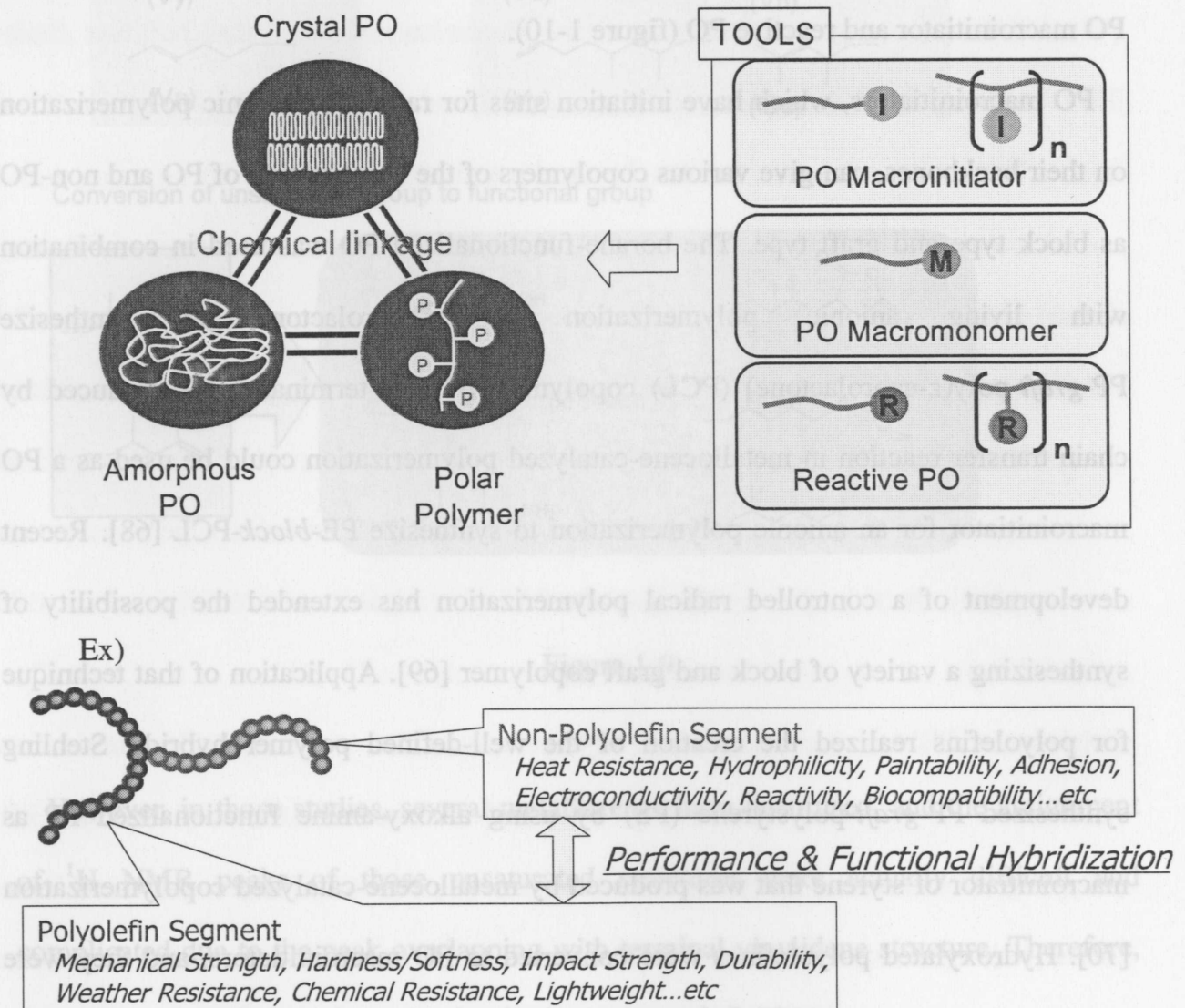


Figure 1-10

PO macromonomers possessing a polymerizable chain end were mentioned above as a useful tool for synthesis of polymer hybrid [53, 54]. Reactive POs having reactive functional groups are considered to be the most conventional way to produce various polymer hybrids. Typically, it is well-known that the maleic anhydride modified POs are useful as a reactive PO to prepare the polymer hybrid [75].

Living polymerization technique is one of the most attractive tools to prepare polymer hybrids based on polyolefins. Yasuda et al. reported several kinds of polymer hybrids consisting of PE, poly(pent-1-ene) and poly(hex-1-ene) as PO segment and PMMA and PCL as non-PO segment [76]. PE-*block*-(ethylene/propylene)copolymer was also prepared by using post-metallocene catalyst systems [77].

As mentioned above, polymer hybrids based on polyolefins have been studied energetically for the creation of high performance polymer materials. Though there are several approaches for it, many studies have only been done by controlled radical polymerization. Therefore, so far, the studies of other approaches have been superficial.

5. Outline of this thesis

The author orients to create functional materials in this thesis. Under the background described above, the author considers that the microstructures, especially unsaturated structures, of polyolefins are very important for a creation of site-selective, namely well-defined, functional polymers, and also that polymer hybrids would be used as functional materials in industry. This thesis concerns the study on microstructures of polyolefins prepared by metallocene catalyst systems to investigate the fine structures of polymers and the polymerization reaction. Furthermore, the syntheses of functionalized

polyolefins, namely polymer hybrids, are also discussed.

In chapter 2, the insertion reaction of functional monomer, 10-undecen-1-ol protected with several kinds of trialkylaluminum (trimethylaluminum, triethylaluminum, tri-n-butylaluminum and triisobutylaluminum), into the metallocene active center of the $\text{En(Ind)}_2\text{ZrCl}_2/\text{MAO}$ catalyst system in the absence of olefin monomers is investigated as a preliminary study related to the copolymerization of functional monomers [82]. Also, the author refers to the effects of the different kinds of alkylaluminum for the insertion reaction of Un-O-AlR_2 into the metallocene active center.

In chapter 3, the unsaturated structures of polyolefins are investigated. At first, the separation of internal and terminal vinylidene peaks of polypropylene in ^1H NMR measurement by making use of the solvent effect is referred [78]. The chain end structures of the polypropylenes produced by three kinds of metallocenes possessing different symmetries ($\text{En(Ind)}_2\text{ZrCl}_2$, as C_2 symmetrical, isopropylidene(cyclopentadienyl)(fluorenyl)zirconiumdichloride ($\text{iPr(Cp)(Flu)ZrCl}_2$), as C_s symmetrical, and Cp_2ZrCl_2 , as asymmetrical) are also discussed [79]. In here, the author studies the assignment of ^1H NMR peaks of unsaturated structures, especially internal vinylidene structure, being actually difficult and complicated due to the peak overlapping with terminal vinylidene structure in polypropylene. The author reports on unsaturated groups in the polymer chain and discuss the mechanism to explain the formation of unsaturated structures. The unsaturated structures in polyhexene families, namely, polyhexene, poly(4-methylpent-1-ene) (4-MP-1) and poly(3-methylpent-1-ene) (3-MP-1), which are seemed as special polymers produced with metallocenes, $\text{En(Ind)}_2\text{ZrCl}_2$ and $\text{iPr(Cp)(Flu)ZrCl}_2$, are also investigated by ^1H NMR analysis [80]. Based on the unsaturated structures in resulting polymers, the influences of the

structures of metallocenes and the kinds of olefin monomers are discussed.

From chapter 4, the author describes the subjects concerning to synthesize polymer hybrids based on polyolefins. Chapter 4 describes the new methodology for synthesizing polyolefinic graft block copolymers taking unsaturated structures and their morphological features [81]. In here, terminally hydroxylated polypropylene (PP) prepared from pyrolyzed PP was used for synthesis of PP-(ethylene/propylene)copolymer hybrid via coupling reaction. The ability of the resulting polymer hybrid as a compatibilizer is also discussed.

In chapter 5, PE-PMMA polymer hybrid was synthesized via reversible addition fragmentation radical transfer (RAFT) polymerization of MMA with PE chain transfer agent (PE-CTA) [83]. The structure of PE-CTA produced by sequential functionalization of terminally hydroxylated PE was confirmed by ^1H NMR and FT-IR analyses. The results of GPC after MMA polymerization revealed that the molecular weight of the resulting polymers increased compared with the one of the PE-CTA. Transmission electron microscopy (TEM) images indicated the nanometer level microphase-separation morphology between the PE segment and PMMA segment.

In chapter 6, polypropylene-*graft*-polystyrene (PP-*g*-PS) was synthesized by the coupling reaction of brominated polypropylene produced by metallocene-catalyzed copolymerization of propylene with 11-bromo-1-undecene and polystyryl lithium salts made by living anionic polymerization as a conventional method. Those structures could be confirmed by ^1H NMR analysis. TEM micrographs of PP-*g*-PS copolymers indicated the nanometer level microphase-separation morphology between the polypropylene segment and polystyrene segment.

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Chapter 2

**Investigation of insertion reaction of 10-undecen-1-ol
protected with alkylaluminum in $\text{En}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$
catalyst system**

1. Introduction

The investigation of elementary reactions in olefin polymerization, such as monomer insertion, chain propagation and termination, has become one of the most important subjects for the synthesis of the precisely controlled polymers [1-4]. Since the discovery of the metallocene catalyst system, as mentioned in chapter 1, a great amount of research on olefin polymerization with metallocene has contributed significantly to the knowledge of these reactions [5-14].

In previous papers, it was shown that metallocene catalyst systems were active in the copolymerization of olefin monomers with polar monomers protected with alkylaluminum [15-24]. Furthermore, recent studies found that alkylaluminum compounds were used in regioselective copolymerization of olefins with polar monomers, such as allyl alcohol and allyl amine, via chain transfer reactions [17, 18, 20]. Needless to say, obtained copolymers possessing polar groups would be regarded as functional polymers. In those papers, it was suggested that the kinds of alkylaluminum, which were used for the protection of functional groups of polar monomers, influence the chain transfer reaction. However, those reactions have been studied only by analysis of the chain structures of the resulting copolymers. Furthermore, the mechanism of the insertion reaction of polar monomers into the metallocene active center has never been clarified. This has led to interest in investigating the reaction of an activated metallocene and polar monomers in the absence of olefin monomers.

The author aimed to investigate the insertion reaction of 10-undecen-1-ol (Un-OH) protected with several kinds of trialkylaluminum (trimethylaluminum, triethylaluminum, tri-*n*-butylaluminum and triisobutylaluminum) into the metallocene active center of the $\text{En}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system in the absence of olefin monomers as a preliminary

study. Also, the author would like to refer to the effects of the different kinds of alkylaluminum for the insertion reaction of Un-O- AlR_2 .

2. Experimental section

Materials

10-Undecen-1-ol (Un-OH) was purchased from Tokyo Kasei Kogyo Co., Ltd. and purified by distillation. Alkylaluminum compounds, which were trimethylaluminum (TMAL), triethylaluminum (TEAL), tri-n-butylaluminum (TNBAL) and triisobutylaluminum (TIBAL), were purchased from Tosoh Finechem Co. and used as received. $\text{En(Ind)}_2\text{ZrCl}_2$ was purchased from Sigma-Aldrich Co.. Methylalminoxane (MAO) was purchased as toluene solution (10wt%) from Albemarle Co. and used without purification. Toluene purchased from Wako Pure Chemical Industries, Ltd. were dried over Sodium metal and distilled before use. Ethylene monomer (Mitsui Chemicals) was used without any further purification. Organometallic compounds were treated under the nitrogen atmosphere. 1-Undecanol, 1-dodecanol, 1-tridecanol, 1-pentadecanol and 1-octadecanol were purchased from Kanto Kagaku Co.. 11-Dodecen-1-ol was purchased from Sigma-Aldrich Co. Those reagents were used as received for gas chromatographic (GC) analysis.

Polymerization procedure of ethylene with Un-O- AlR_2

Polymerization experiments were carried out in 500 ml glass flasks each equipped with a mechanical stirrer, a thermocouple and a monomer inlet tube. Toluene (450 ml) was introduced into the reactor. Un-OH (2.0 mmol) pretreated with aluminum compounds (TMAL, TEAL and TIBAL; 2.2 mmol) for 15 minutes was added to the

reactor, and then, $\text{En}(\text{Ind})_2\text{ZrCl}_2$ (0.10 mmol) activated by MAO (10 mmol [Al]) for 30 minutes was added to the reactor. The reaction mixture was stirred for 10 minutes in the reactor. Then, the polymerization was started by introduction of an ethylene monomer into the reactor at 25 °C. This temperature was kept during the polymerization under the constant feed, 0.3 NL/h, of monomer gas. After 60 min, 50 mL of methanol was added to the reactor in order to terminate the polymerization. The reaction mixture was poured into 1 L of methanol. Polymers were collected by filtration and washed with 500 ml of methanol, then dried under the reduced pressure at 80 °C for 10 hr.

Reaction of $\text{En}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ and Un-O-AlR_2

Un-OH (10 mmol) was treated with trialkylaluminum (20 mmol) in decane (20 ml) at room temperature for 15 minutes to prepare alkylaluminum-protected Un-OH (Un-O-AlR_2) before the reaction. In a 30 ml Schlenk flask was placed 41.9 mg of $\text{En}(\text{Ind})_2\text{ZrCl}_2$ (0.10 mmol) and toluene solution of MAO (6.52 ml; 10 mmol as [Al]) to activate metallocene in toluene. Un-O-AlR₂ (1.0 mmol) and excess trialkylaluminum in decane was added to the flask at room temperature. Each sample solution was poured into 10 ml of HCl aq (1 N) solution. Then, the organic phase was separated and subjected to GC analysis.

Analysis

Analysis of polymers

Molecular weights and molecular weight distributions were determined by gel-permeation chromatography (GPC; Waters, Alliance GPC 2000) using o-dichlorobenzene as solvent at 140 °C. ¹H NMR spectra were recorded on a JEOL

JNM GX-400 series spectrometer operated at 400 MHz in the pulse Fourier transform mode. Instrumental conditions were as follows: pulse angle, 45 °; pulse repetition, 5.0 sec; spectral width, 18050 Hz; temperature, 110 °C; data points, 20000. Polymer solutions used for NMR were prepared by dissolving 50 mg of polymer in 0.5 ml of ODCB as solvent.

Analysis of reaction samples

GC chart was recorded on a Shimadzu GC-1700 chromatograph with a capillary column DB-17 (0.25 mm x 30 m, carrier gas; helium, flow rate; 76.7 ml/min., split ratio; 1:30), J&W Scientific Inc. Measurement conditions were as follows: initial temperature; 150 °C for 15 min., rate; 10 °C/min., final temperature; 250 °C for 20 min., injection column temperature; 250 °C. Acetone was used as solvent for measurement. The resulting organic phase was diluted by acetone, and that solution was used for GC analysis.

Products were identified by comparison with authentic samples. 1-undecanol, Rt = 10.40 minutes. 10-undecen-1-ol, Rt = 10.82 minutes. 1-dodecanol, Rt = 15.56 minutes. 11-dodecen-1-ol, Rt = 16.22 minutes. 1-tridecanol, Rt = 19.08 minutes. 1-pentadecanol, Rt = 23.66 minutes. 1-octadecanol, Rt = 26.68 minutes.

Gas chromatography - mass spectrometric (GC-MS) analysis was conducted on a Hewlett-Packard HP6890 / HP5973 with using a capillary column DB-17 (0.25 mm x 30 m, carrier gas; helium, flow rate; 1.0 ml/min., split ratio; 1:10), J&W Scientific Inc. Measurement conditions were as follows: initial temperature; 50 °C, rate; 10 °C/min., final temperature; 250 °C for 40 min., injection column temperature; 250 °C. The organic phase was diluted by acetone, and the solution was used for GC analysis.

^{13}C NMR spectra were recorded on a JEOL ECP-500 spectrometer operated at 125 MHz in the pulse Fourier transform mode. For ^{13}C -NMR instrumental conditions were as follows: pulse angle, 45° ; pulse repetition, 8.0 sec; spectral width, 32000 Hz; temperature, 27°C . For DEPT (distortionless enhancement by polarization transfer), the DEPT135 spectrum was measured. Used sample solutions for NMR was prepared by dissolving 50 mg of sample in 0.5 ml of chloroform- d_3 (CDCl_3) as solvent.

3. Results and discussion

Confirmation of incorporation of Un-O-AlR₂ in Polyethylene

In here, $\text{En}(\text{Ind})_2\text{ZrCl}_2$ activated with MAO was used as a metallocene catalyst. First, to confirm the insertion of Un-O-AlR₂ into the metallocene active center, copolymerizations of Un-OH protected with trialkylaluminum (Un-O-AlR₂) were carried out in the presence of an ethylene monomer using an $\text{En}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system in toluene under atmospheric pressure. The resulting polymers were analyzed by NMR and GPC referring to previous papers [17, 21]. Table 2-1 shows the results of copolymerization conducted using different trialkylaluminums. The incorporation of Un-O-AlR₂ into polyethylene was confirmed in each copolymer, indicating that the Un-O-AlR₂ was inserted into the examined metallocene active center in the presence of olefin monomer.

Table 2-1 Results of copolymerization of ethylene with Un-OH capped with AlR₃^{a)}

Entry	AlR ₃	Yield (g)	M_w ^{b)} (x 10 ⁻³)	M_w/M_n ^{b)}	Un-OH Cont. ^{c)} (mol%)
1	TMAL	0.321	18.5	2.22	0.79
2	TEAL	0.355	5.2	1.97	0.65
3	TIBAL	0.368	7.7	1.93	0.40

a) Polymerization condition; En(Ind)₂ZrCl₂ (0.1 mmol), MAO (10 mmol), AlR₃ (0.22 mmol), Un-OH (0.2 mmol), ethylene (0.3 NL/h), 25 °C, 0.1 MPa. in toluene (400 ml) for 1 hr. b) GPC data, PE standard. c) Estimated by NMR analysis.

Insertion reaction of Un-O-AlR₂ into the metallocene active center in the absence of olefin monomers

The investigation of the insertion reaction of Un-O-AlR₂ into the metallocene active center was conducted using En(Ind)₂ZrCl₂ activated with MAO in the absence of olefin monomers. Un-OH was selected as the monomer in this study because of the tendency preventing monomer propagation reaction compared with other higher α -olefins [21, 25]. Un-OH (1.0 mmol) was pretreated with 2.0 mmol of trialkylaluminum compounds, which were trimethylaluminum (TMAL), triethylaluminum (TEAL), tri-n-butylaluminum (TNBAL) and triisobutylaluminum (TIBAL), to protect the hydroxyl group. En(Ind)₂ZrCl₂ was pretreated with MAO for 30 minutes to prepare the alkyl complex of metallocene. The prepared Un-O-AlR₂ and excess trialkylaluminum were treated with the En(Ind)₂ZrCl₂/MAO system in toluene (15.3 mmol[Zr]/L). The

molar ratios of [OH]/[Zr] were 10/1 in this reaction. After quenching the reactant with hydrochloric acid, the organic phase was separated.

The resulting alcohol compounds were identified by GC analysis through the comparison with authentic samples. GC-MS was also used to distinguish saturated and unsaturated ones. The GC chart in the case of TEAL is shown as a typical example in figure 2-1. The results are summarized in table 2-2.

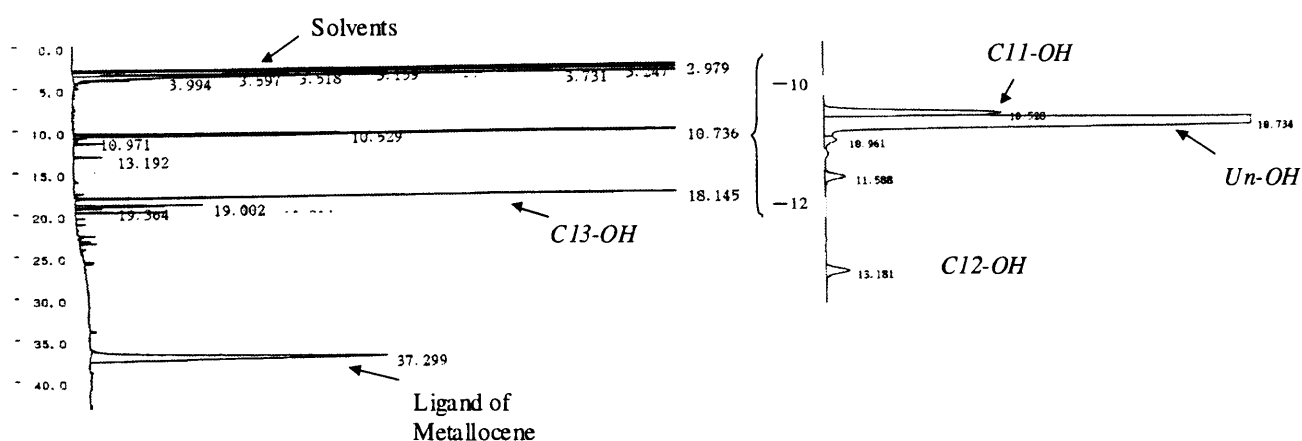


Figure 2-1 GC chart of compounds resulting from TEAL (after 5 min.)

All alcohol compounds were saturated ones except Un-OH (starting material). Those were undecanol (C11-OH; saturated Un-OH) and other alcohol compounds in which alkyl groups derived from trialkylaluminum were incorporated into Un-OH. Namely, for TMAL and TEAL, C12-OH and C13-OH were produced, respectively. For TNBAL and TIBAL, C15-OH was produced. Neither dimer nor oligomers of Un-OH were detected.

Table 2-2 Mol % of identified alcohol compounds formed by the reaction of 10-undecen-1-ol protected with alkylaluminum in $\text{En}(\text{Ind})_2\text{ZrCl}_2 / \text{MAO}$ catalyst system^{a)}

Entry	AlR ₃	Reaction Time (min.)	Undecenol	Undecanol	Dodecenol	Dodecanol	Tridecanol	Pentadecanol
			Un-OH (A)	C ₁₁ -OH (B)	C ₁₂ "-OH (C)	C ₁₂ -OH (D)	C ₁₃ -OH (E)	C ₁₅ -OH (F)
1	TMAL	5	97	1	trace ^{b)}	2	0	0
2		10	95	1	1	3	0	0
3		30	95	1	1	3	0	0
4		60	95	1	1	3	0	0
5		120	95	1	1	3	0	0
6	TEAL	5	73	7	trace ^{b)}	1	19	0
7		10	55	12	trace ^{b)}	1	32	0
8		30	8	20	trace ^{b)}	1	71	0
9		60	0	21	trace ^{b)}	1	78	0
10		120	0	21	trace ^{b)}	1	78	0
11	TNBAL	5	0	45	trace ^{b)}	1	0	54
12		10	0	45	trace ^{b)}	1	0	54
13		30	0	45	trace ^{b)}	1	0	54
14		60	0	45	trace ^{b)}	1	0	54
15		120	0	45	trace ^{b)}	1	0	54
16	TIBAL	5	1	91	trace ^{b)}	1	0	7
17		10	0	91	trace ^{b)}	1	0	8
18		30	0	91	trace ^{b)}	1	0	8
19		60	0	91	trace ^{b)}	1	0	8
20		120	0	91	trace ^{b)}	1	0	8

a) Estimated by GC analysis. b) Less than 0.5 mol%.

Figure 2-2 shows the relations of the molar ratios of Un-OH and reaction time. This figure indicates the consumption rates of Un-O-AlR₂ for each alkylaluminum, and the order was TNBAL, TIBAL>TEAL>>TMAL. For TNBAL and TIBAL, almost all of Un-O-AlR₂ was consumed in 5 minutes. For TMAL, however, its consumption was limited. For TEAL, it was consumed gradually. Although 10 times as much amount of Un-OH (or resulting Un-O-AlR₂) as En(Ind)₂ZrCl₂ was used, all of Un-O-AlR₂ was completely consumed for TEAL, TNBAL and TIBAL, indicating that Un-O-AlR₂ was reacted catalytically.

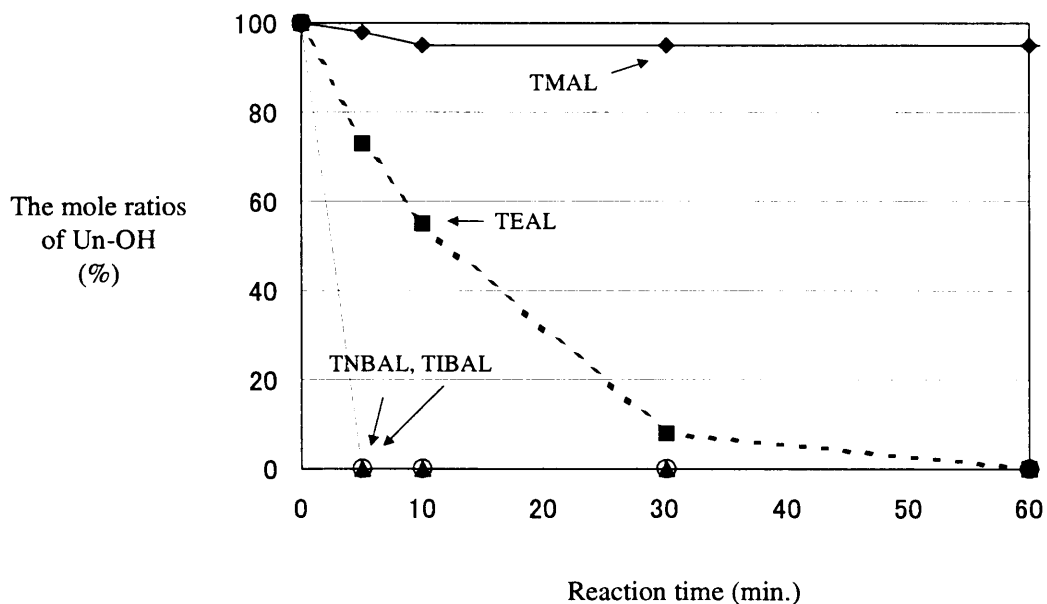


Figure 2-2 Relations of mole ratios of Un-OH and reaction time

In expanded ¹³C and DEPT NMR spectra of entry 10 for TEAL (figure 2-3), the signals were assigned as the methine carbon appeared around 30.0 ppm and 34.5 ppm.

Those peaks would be due to branched alkyl groups as like structures **A** and **B**. It would be considered that those branched alcohol compounds were formed by the insertion of Un-O-AlR₂ followed by alkyl exchange reactions with trialkylaluminum as shown in figure 2-4.

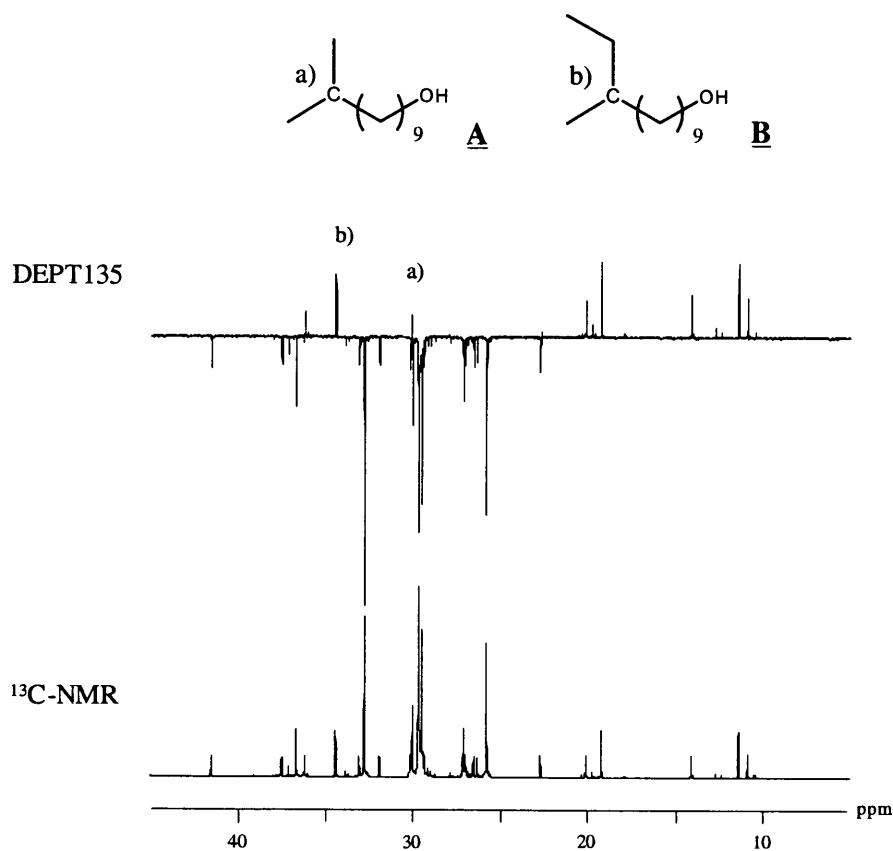


Figure 2-3 Expanded ¹³C and DEPT NMR spectra (recorded in CDCl₃ at 27 °C) between 5 and 45 ppm of entry 10

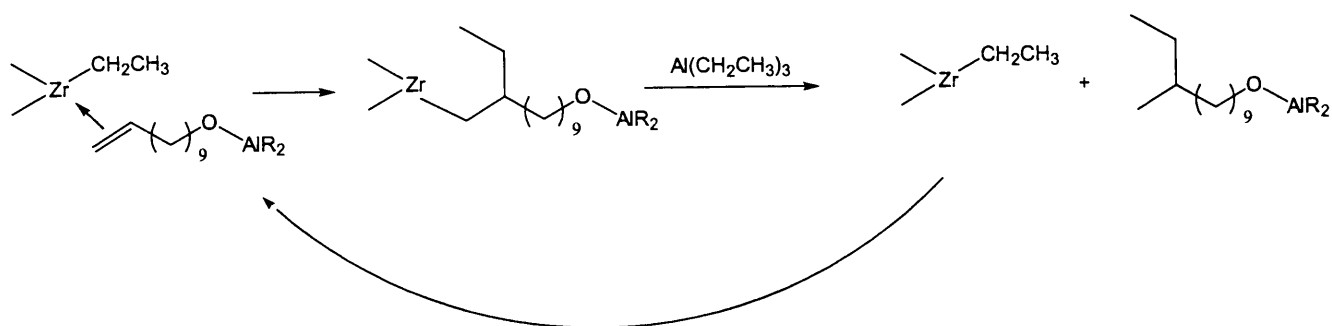


Figure 2-4 Alkyl exchange reaction in the case of TEAL

Each alcohol compound would be formed via the insertion reaction of Un-O-AlR₂ into the metallocene active center as shown in figure 2-5. Compounds D, E, and F, which were the alkyl-added ones to Un-OH, would be formed via route 6 after an insertion of Un-O-AlR₂ into the Zr-R (*a*) active center formed by the reaction of En(Ind)₂ZrCl₂ with MAO or by alkyl exchange reaction. Undecanol (B) would be formed via route 7 after an insertion of Un-O-AlR₂ into Zr-H (*c*) active center formed by the elimination of alkene from Zr-R (route 2). The compound C produced from (*b*) (route 5) was negligible. Neither dimer nor oligomers of Un-OH were produced, indicating that further insertion of Un-O-AlR₂ would not occur at (*b*) and (*d*).

In the case of TMAL, the consumption of Un-OH was low. The reason might be that the alkyl exchange reactions after the insertion of Un-O-AlR₂ hardly occur or that the insertion of Un-O-AlR₂ is prevented due to coordination of the oxygen atom of the monomer to the metallocene active center because TMAL is not bulky enough. For

TEAL, E was found mainly, indicating that the reaction progressed via route *1-6*. In the case of TNBAL, B and F were found in the same amounts, which would indicate that reactions both via route *1-6* and via route *2-3-7* might occur competitively. For TIBAL, since B was formed mainly, the reaction via route *2-3-7* would progress dominantly. In all examples, D was hardly detected although MAO was used in large amounts, therefore, the alkyl exchange reaction (route *6*) with MAO would hardly occur.

Thus, for TEAL, TNBAL and TIBAL, the insertion reaction of Un-O-AIR₂ would progress catalytically via route *1-6* or route *2-3-7*. The priority of the routes might depend on the ease of the elimination of alkene from Zr-R (route *2*), namely the ease of the proton transfer to active center; -CH₂**CH**(CH₃)₂ in TIBAL > -CH₂**CH**₂CH₂CH₃ in TNBAL > -CH₂**CH**₃ in TEAL.

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Chapter 3

Microstructures of polyolefins prepared by metallocene catalyst systems

Preface;

The analysis of microstructures of polyolefins is of particular interest to scientists and engineers gaining a deeper understand the polymerization mechanism and the properties of them [1-20]. Especially, the study on the chain end structure of polyolefins is one of the most interesting subjects because it provides important key information on the elucidation of propagation and termination mechanisms in olefin polymerization. And also, the end structure often acts as a useful functional group in order to create new functional polyolefins. Furthermore, unsaturated chain end groups could be utilized for addition of polar or other functional groups [21-25].

The study on the effect of magnesium supported titanium catalysts for the chain end structures of polypropylene have been reported with NMR analysis [26, 27]. For instance, the initiation reaction of propylene polymerization has been regarded as 1,2-insertion of a monomer by the detection of n-propyl group as the usual initial chain end structure of the polymer [11-17]. In the case of metallocene-catalyzed propylene polymerization, the termination reactions of the polymer chain are believed to be a derivative of the transfer of a β -hydrogen or a methyl group of the growing polymer chain owing to the detection of vinylidene, vinyl and vinylene groups as unsaturated chain end structures. In previous reports, it was indicated that chain end structures depend on the species of the catalysts. However, the effect of symmetry of the catalyst on chain propagation and a termination reaction has never been clarified.

In here, the author aimed to investigate the maicrostructures, especially unsaturated structures, in polyolefins in order to contribute to understanding of polymerization mechanism and to creation of functional polymers.

3.1. The detailed analysis of the vinylidene structure of metallocene-catalyzed polypropylene

1. Introduction

Since the discovery of metallocene catalyst system, the field of olefin polymerization has been extended from technology to science due to a homogeneous active site of the catalyst. And, it is well known that the metallocene-catalyzed PP has vinylidene end group produced by β -hydride elimination [11, 28]. Recently, the terminal chain end structures such as vinyl, butenyl and isobutenyl structures have been reported on polypropylene prepared by metallocenes that had different ligand structures [17, 29]. However, the assignment of ^1H NMR peaks of those unsaturated structures, especially internal vinylidene structure, is actually difficult and complicated due to the peak overlapping with terminal vinylidene structure in polypropylene [4, 14]. The author, at first, aimed to study on the separation of internal and terminal vinylidene peaks of polypropylene in ^1H NMR measurement by making use of the solvent effect, and the comparison of the amounts of those vinylidene structures between $\text{En}(\text{Ind})_2\text{ZrCl}_2$, which is C_2 symmetrical, and $\text{iPr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$, which is C_s symmetrical, too.

2. Experimental section

Materials

Tetrahydrofuran (THF) and pentane purchased from Wako Pure Chemical Industries, Ltd. were dried over Sodium metal and distilled before use. Methylene chloride purchased from Wako Pure Chemical Industries, Ltd. were dried over CaH_2 and distilled before use. n-Butyllithium (n-BuLi) was purchased from Wako Pure Chemical Industries,

Ltd. as hexane solution (1.6 mol/L). 6,6-Dimethylfulvene was purchased from Sigma-Aldrich Co. and used without purification. Fluorene and zirconium tetrachloride (ZrCl_4) were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Propylene monomer (Mitsui Chemicals) was used without any further purification. Other materials were same as described in section 2. Organometallic compounds were treated under the nitrogen atmosphere.

Preparation of $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$

$i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ was prepared according to the literature [30]. At first, 2-(cyclopentadienyl)-2-fluorenylpropane (**A**) was prepared, and then, $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ was prepared by a metallation reaction. The reaction was operated under nitrogen atmosphere (shown in figure 3-1).

In a 500 ml round bottom flask was placed 60 mmol (9.98 g) of fluorene dissolved in 100 ml of THF. To this solution an equimolar amount of n-BuLi was added over 30 min. at ambient temperature. The resulting red solution was stirred for 4 hour. To this solution 60 mmol of 6,6-dimethylfulvene (6.37 g) in 50 ml of THF was added at ambient temperature. After stirring for 4 hour, the reaction was quenched by adding 30 ml of an aqueous solution of saturated ammonium chloride. The organic phase was separated and dried over magnesium sulfate. After evaporation of the solvent, a white solid was obtained. It was purified by column chromatography over silica gel (eluent; hexane) to yield 13.08 g (80 %) of white solid as (**A**).

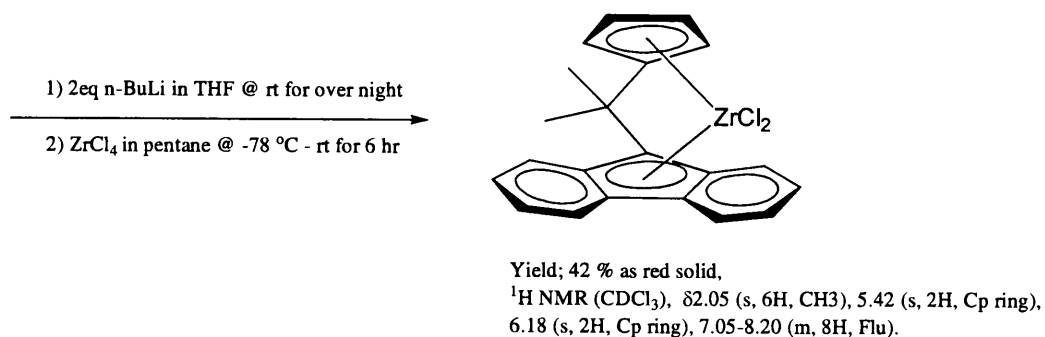
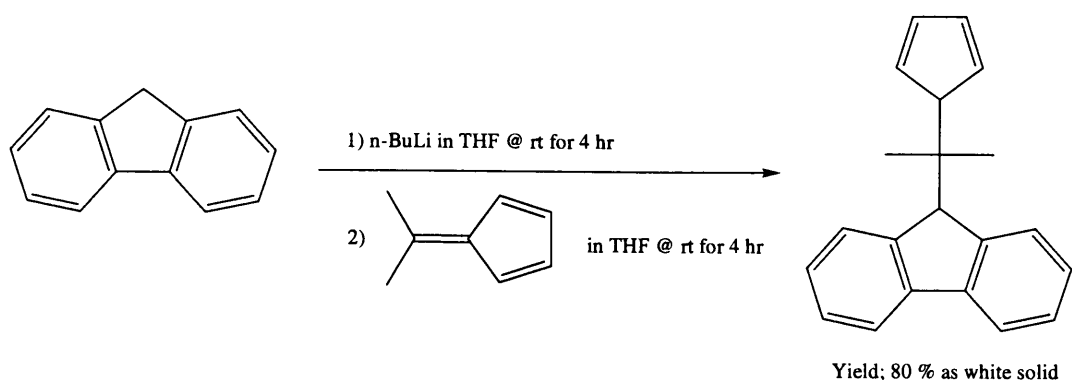


Figure 3-1

A 500 ml round bottom flask was charged with 35 mmol (A) (5.82 g) in 200 ml of THF. To this solution 70 mmol of n-BuLi was added dropwise at room temperature. The resulting red solution was stirred overnight. The evaporation of the solvent gave an orange solid as a dianionic ligand. To a suspension of the dianionic ligand in 200ml of pentane in a 1 l round bottom flask was added a suspension of 35 mmol of $ZrCl_4$ powder (8.16 g) in 200 ml of pentane at $-78\text{ }^\circ\text{C}$. The mixture was stirred for 6 hour at ambient temperature. The reaction mixture was filtered and obtained orange solid was extracted with methylene chloride. After recrystallization with methylene chloride, 4.81

g of red solid was obtained as $iPr(Cp)(Flu)ZrCl_2$ (42 %).

1H NMR ($CDCl_3$), δ 2.05 (*s*, 6H, CH_3), 5.42 (*s*, 2H, Cp ring), 6.18 (*s*, 2H, Cp ring), 7.05-8.20 (*m*, 8H, Flu).

Polymerization

All polymerization experiments were carried out in 500 ml of glass flasks equipped with mechanical stirrer, thermocouples and monomer inlet tube. Into the reactor, 250 ml of dry toluene was introduced and saturated with propylene monomer gas. After heating the solvent to, 70 °C, MAO in toluene (5 mmol as Al atom) was added in the reactor, and then, the polymerization was started by addition of metallocene (0.005 mmol) in the reactor. That temperature was kept for 30 min. under the constant feed, 100 NL/h, of monomer gas. After that, 5 mL of isobutanol was added to the reactor in order to terminate the polymerization. The reaction mixture was poured in 1 L of methanol. Resulting polymers were obtained by filtration and washed with methanol, then dried under the reduced pressure at 80 °C for 10 hours. 12.86 g of polypropylene (PP-1) was produced by using $En(Ind)_2ZrCl_2$, and 2.33 g of polypropylene (PP-2) was produced by using $iPr(Cp)(Flu)ZrCl_2$.

Analysis of polymer

1H NMR spectra were recorded on a JEOL GSX-400 spectrometer operating at 400 MHz in Fourier transform mode. Instrument conditions were as follows: pulse angle, 45°; pulse repetition, 5.0 sec; spectral width, 8000 Hz; temperature, 118 °C; data points, 32k. The NMR samples were prepared by dissolving 50 mg of polymer in 0.5 ml of decahydronaphthalene- d_{18} (Decalin) or 1,2-dichlorobenzene- d_4 (ODCB) as solvent.

3. Results and discussion

Two metallocenes, $\text{En}(\text{Ind})_2\text{ZrCl}_2$, **1**, and $\text{iPr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$, **2**, were chosen in this study as typical C_2 and C_s symmetrical ones. Those metallocenes could produce isotactic polypropylene and syndiotactic polypropylene, respectively. Vinylidene structures of PP-1 obtained by **1** and PP-2 by **2** were investigated by ^1H NMR. In previous paper [31], it was mentioned that the terminal vinylidene structure changed to isobutenyl structure in case of using 1,1,2,2-tetrachloroethane- d_2 (TCE) as a solvent. Therefore, at first, decalin was used for the NMR measurement as a solvent. The NMR spectra of the vinylidene protons (4.50-4.80 ppm) were shown in figure 3-2. The peaks were assigned as follows [4, 14, 17, 29]. The terminal vinylidene protons were observed at 4.62 and 4.69 ppm, respectively, because these two protons were in the different chemical environment. On the other hand, the internal vinylidene protons resonated at the same position of around 4.70 ppm. It was remarkable in PP-2 that the peak was more intense than the higher field one because of overlapping with the lower field peak of the terminal vinylidene protons like as same as using TCE. Since that made the analysis complicated, we tried to make the peak separation, making use of the solvent effect induced by an aromatic compound. The ^1H NMR spectra of PP-1 and PP-2 observed in ODCB solution were presented in figure 3-3. It was noticeable that new peaks were observed in the range of 4.68 and 4.74 ppm in PP-2. We assigned the peaks at 4.69 and 4.71 ppm to the vinylidene protons adjacent to the chain end, where two vinylidene protons were in the slightly different chemical environment, and the lowest peak (4.74 ppm) to other internal vinylidene protons, respectively. The terminal vinylidene peaks at 4.61 and 4.67 ppm had the equal intensity, because internal

vinylidene peaks were removed from the overlapping ones of vinylidene. Internal vinylidene might be produced via an allyl complex that was proposed by Schaverien [29].

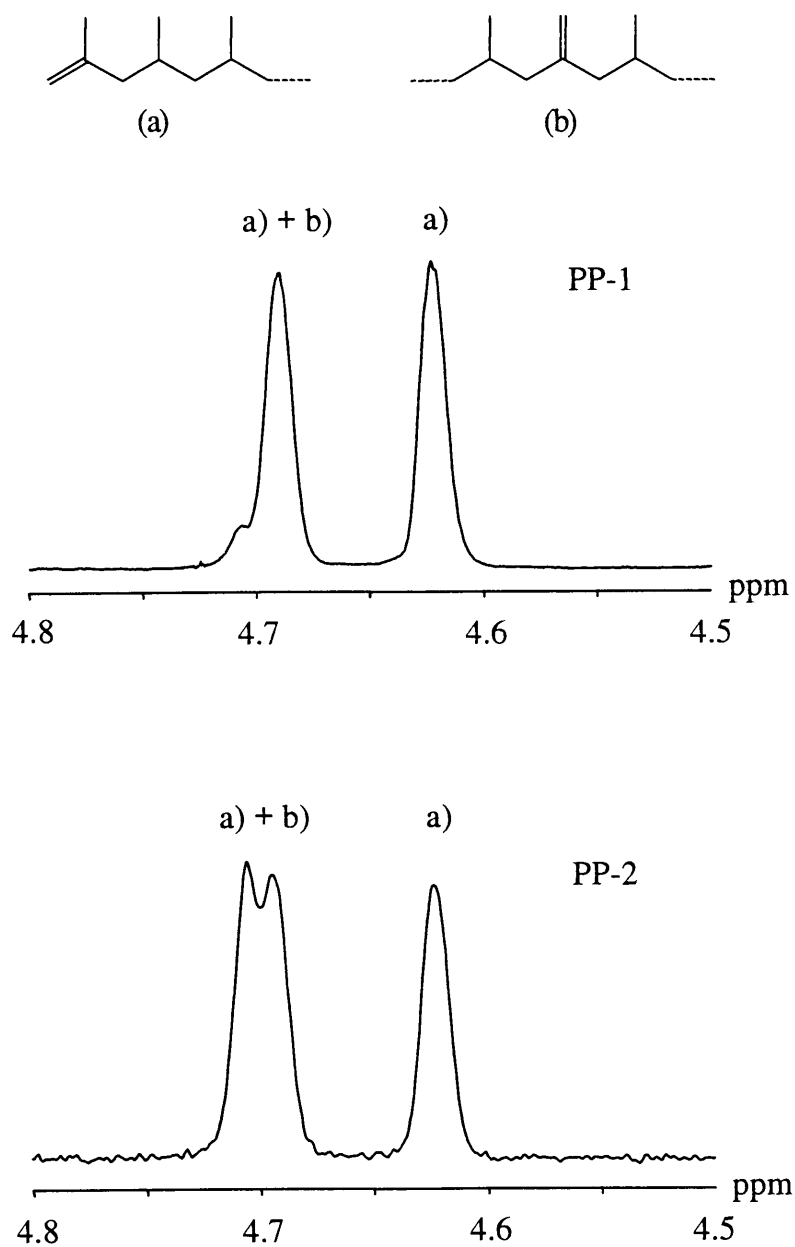


Figure 3-2 Expanded ¹H NMR spectra between 4.5 and 4.8 ppm of PP-1 and PP-2 in Decalin

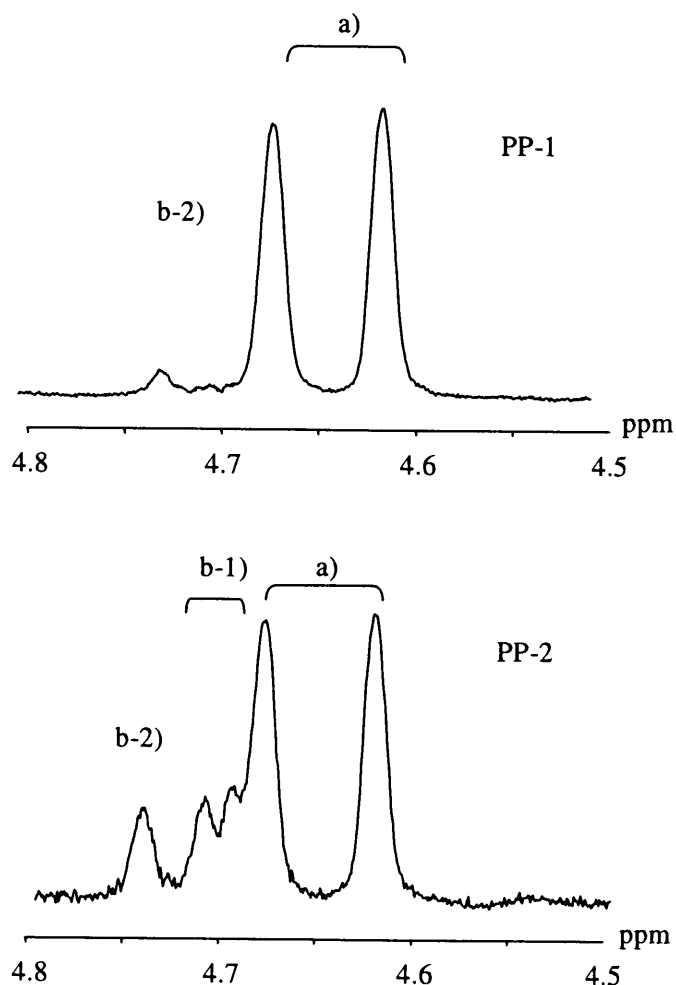


Figure 3-3 Expanded ¹H NMR spectra between 4.5 and 4.8 ppm of PP-1 and PP-2 in *o*-dichlorobenzene

The three types of vinylidene structures, which were confirmed by this study, were shown in figure 3-4. From the spectra in figure 3-3, three vinylidene structures, that is, Vd(a), Vd(b-1) and Vd(b-2), existed with the ratio of 92:3:5 in PP-1 and 60:31:9 in PP-2, indicating that the internal vinylidene structure was formed with the higher frequency

with 2 than with 1.

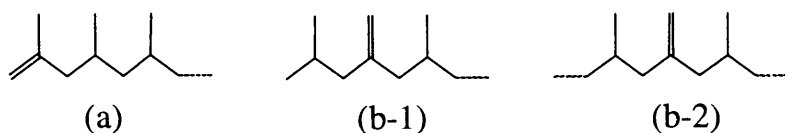


Figure 3-4 Structures of vinylidene groups

4. Conclusion

The vinylidene structures in metallocene-catalyzed polypropylenes were analyzed by ^1H NMR. The internal and terminal vinylidene structures were clearly distinguished using ODCB as solvent due to the effect of the ring current, and the vinylidene structure next to the chain end could be assigned for the first time as different peaks from the other vinylidene structures. $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ tended to produce internal vinylidene structures compared with $\text{En}(\text{Ind})_2\text{ZrCl}_2$.

3.2. Chain end structures of polypropylenes prepared with different symmetrical metallocene catalysts

1. Introduction

In previous reports, it was indicated that chain end structures depend on the species of the catalysts [25-28]. However, the effect of symmetry of the catalyst on chain propagation and a termination reaction has never been clarified. This has led to interest in investigating detailed saturated and unsaturated structures of polypropylenes produced with different symmetrical metallocenes.

In here, three kinds of metallocenes, $\text{En}(\text{Ind})_2\text{ZrCl}_2$ as C_2 symmetrical, $\text{iPr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ as C_s symmetrical, and Cp_2ZrCl_2 as asymmetrical, were selected to discuss the chain end structures of the resulting polypropylenes. The author reports on unsaturated groups in the polymer chain and discuss the mechanism to explain the formation of unsaturated structures.

2. Experimental section

Materials

Cp_2ZrCl_2 purchased from Wako Pure Chemical Industries, Ltd. was used as received. Other materials were same as described in section 3-1.

Polymerization

All polymerization experiments were carried out in 500 ml glass flasks equipped with mechanical stirrer, thermocouple and monomer inlet tube. 250 ml of dry toluene was added to the reactor, and monomer gas was introduced in the reactor through the inlet

tube. After heating the solvent to polymerization temperature, MAO in toluene (5 mmol [Al]) was added in the reactor, and then, the polymerization was started by addition of 5 ml of toluene solution dissolved metallocene (0.005 mmol) in the reactor. That temperature was maintained during the polymerization under the constant feed of 100NL/h of propylene monomer gas. After that, 5 mL of isobutanol was added to the reactor in order to terminate the polymerization. The reaction mixture was poured in 1 L of methanol. Polymers (PP2-5) were corrected by filtration and washed with 500 ml of methanol, then dried under reduced pressure at 80 °C for 10 hrs. Polymer (PP1) was separated from methanol by decantation and washed with methanol several times, then dried under reduced pressure at 80 °C for 10 hrs.

Analysis of polymer

Molecular weights and molecular weight distributions were determined by gel-permeation chromatography (GPC) using *o*-dichlorobenzene as solvent. ¹³C NMR spectra were recorded on a JEOL JNM GSX-400 series spectrometer operated at 100 MHz in pulse Fourier transform mode. Instrument conditions were as follows: pulse angle, 45 °; pulse repetition, 5.0 sec; spectral width, 18050 Hz; temperature, 118 °C; data points, 32768. ¹H NMR spectra were recorded on a JEOL JNM GSX-400 series in pulse Fourier transform mode. Instrument conditions were as follows: pulse angle, 45 °; pulse repetition, 5.0 sec; spectral width, 8000 Hz; temperature, 118 °C; data points, 32768. Polymer solutions used for NMR were prepared by dissolving 50 mg of polymer sample in 0.5 ml of ODCB or of Decalin as solvents.

3. Results and discussion

Polymerizations were conducted using three kinds of metallocenes activated with excess amount of MAO in toluene under atmospheric propylene gas feeding at a constant rate. Chain end structures of the resulting polymers were identified by ^1H and ^{13}C NMR with ODCB or Decalin as a solvent to restrain the isomerization of vinylidene group to isobutenyl group during the measurement [31]. The results of polymerization and the data of identified groups are summarized in table 3-1. Expanded ^1H NMR and ^{13}C NMR spectra of resulting polymers (PP3 and PP5) in ODCB are shown in figure 3-5 and 3-6 with assigned structures according to previous reports [28-31], respectively. And possible pathways to form each structure are shown in schemes (1)-(12) in figure 3-7.

On the basis of the previous papers described the assignment of NMR spectra [26-29], 1,2-inserted chain end could lead to vinylidene group (A), n-propyl group (G) and i-propyl group (H) as described in schemes (1)-(3) in figure 3-7. 2,1-inserted active chain end could give 2-butenyl group (C), n-propyl group (G), i-propyl group (H) and n-butyl group (I) as schemes (5)-(7). i-Butenyl group (B) and 4-butenyl group (D) are mentioned as being derive from the isomerization as shown in schemes (4) and (8) [14]. By allylic activation of the polymer chain, internal vinylidenes (E, F) would be generated as shown in schemes (9) and (10) [16]. i-Propyl group (H) also derives from the 1,2-insertion of a monomer into the Zr-CH₃ bond as shown in scheme (11). Ethyl group (J) by 2,1-insertion of a monomer into the Zr-CH₃ bond is negligible for a small amount in this study.

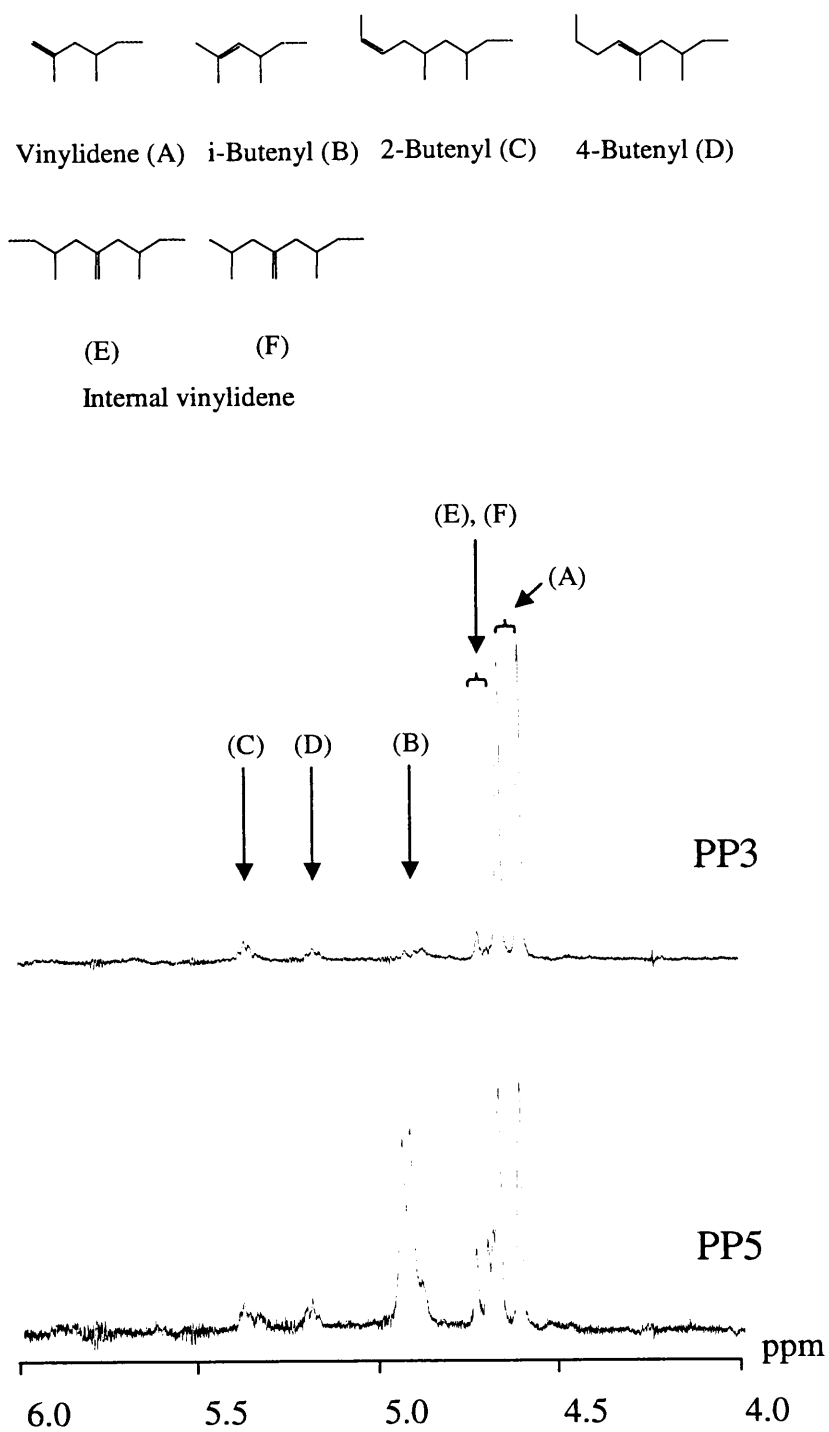


Figure 3-5 Expanded ^1H NMR spectra (recorded in ODCB at 118°C) of the olefinic region of the PP2 and PP5

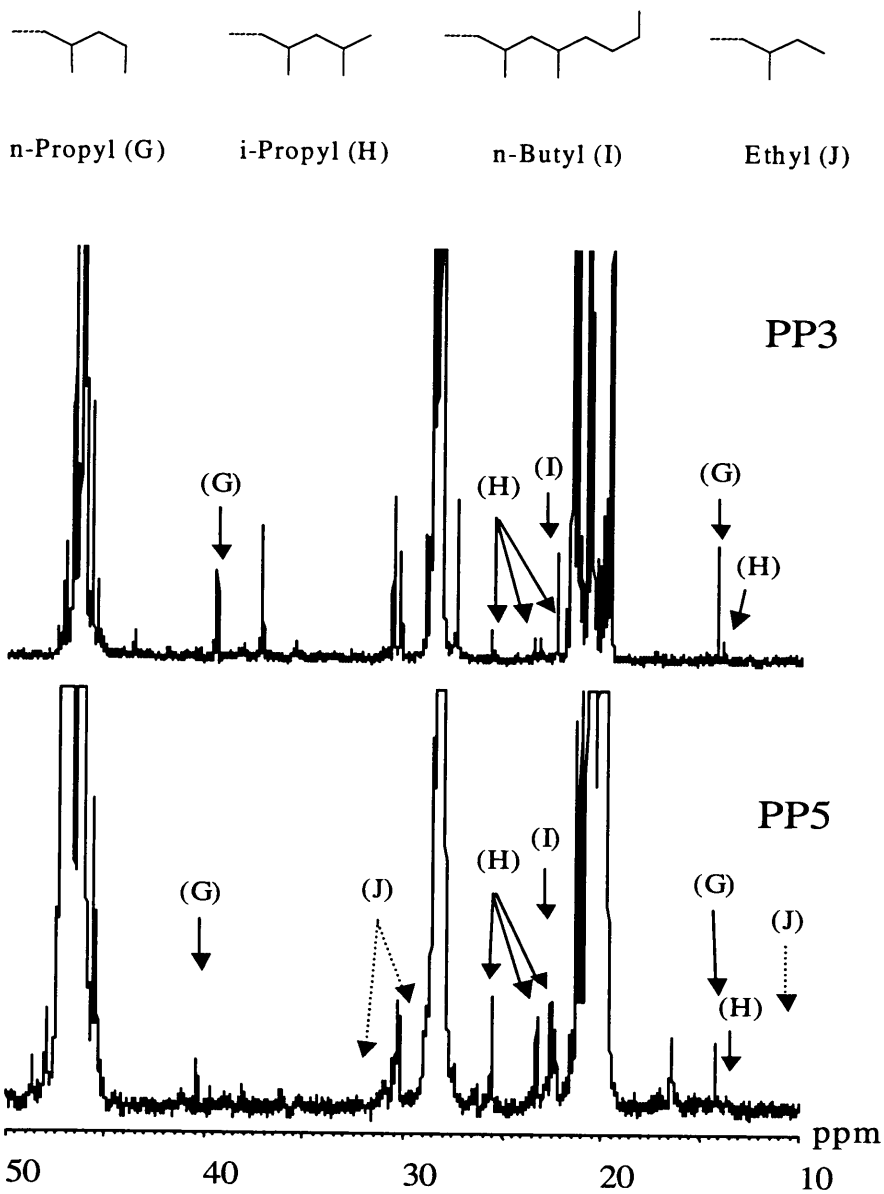


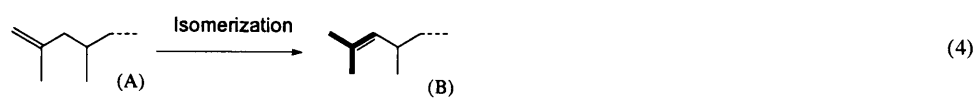
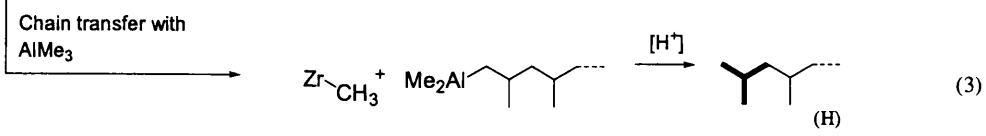
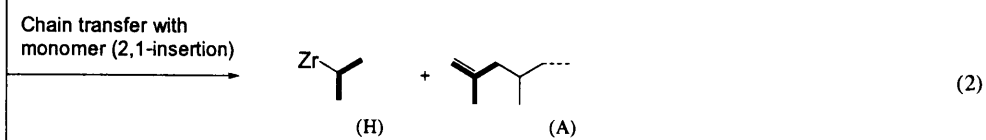
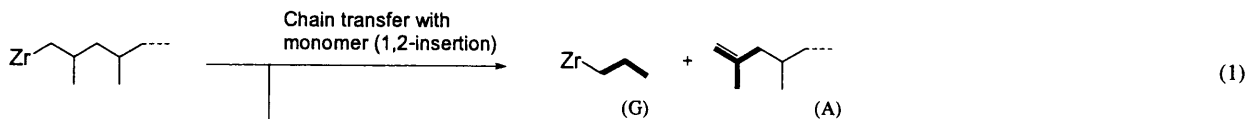
Figure 3-6 Expanded ^{13}C NMR spectra (recorded in Decalin at 118°C) between 10 and 50 ppm of the PP2 and PP5

Table 3-1 Results of propylene polymerization^{a)}

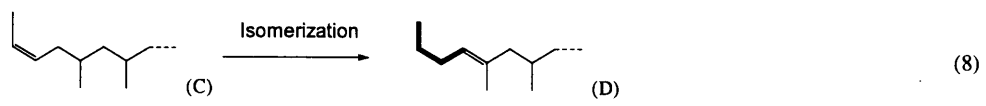
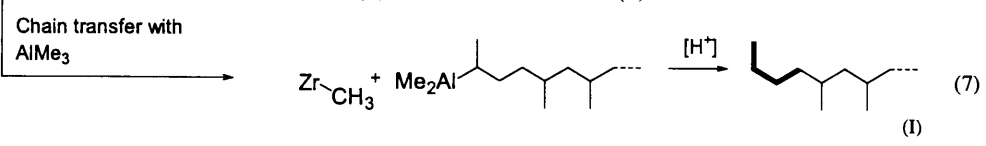
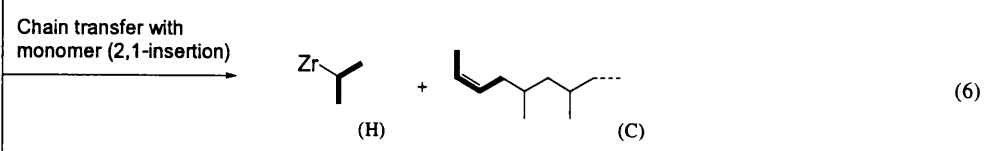
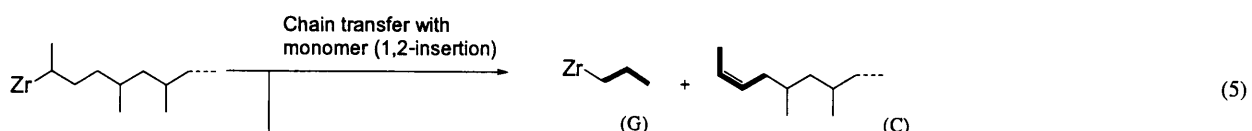
Run#	Metallocene	Polymn. Temp. (°C)	Activity ^{b)}	M_n ^{c)}	Unsaturated and saturated groups in polymer (unit mol%) ^{d)} In brackets, percentages of units (A-J) in each polymer									
					Unsaturated						Saturated			
					(A) Vinylidene	(B) i--Butenyl	(C) 2-Butenyl	(D) 4-Butenyl	(E) (Internal vinylidene)	(F)	(G) n-Propyl	(H) i-Propyl	(I) n-Butyl	(J) Ethyl
PP1	Cp2ZrCl2	25	1762	2371	1.28 (48.5)	-	0.04 (1.5)	-	-	-	1.32 (50.0)	-	-	-
PP2	En(Ind) ₂ ZrCl ₂	50	8984	9907	0.14 (17.3)	0.04 (4.9)	0.07 (8.6)	0.06 (7.4)	0.02 (2.5)	0.01 (1.2)	0.26 (32.1)	0.11 (13.6)	0.10 (12.4)	-
PP3	En(Ind) ₂ ZrCl ₂	70	5144	3962	0.72 (33.2)	0.10 (4.6)	0.06 (2.8)	0.07 (3.2)	0.04 (1.8)	0.03 (1.4)	0.78 (35.9)	0.14 (6.5)	0.23 (10.6)	-
PP4	iPr(Cp)(Flu)ZrCl ₂	50	672	26423	0.09 (12.2)	0.31 (41.8)	0.04 (5.3)	0.03 (4.1)	0.03 (4.1)	0.03 (4.1)	0.05 (6.7)	0.13 (17.6)	0.03 (4.1)	trace ^{e)}
PP5	iPr(Cp)(Flu)ZrCl ₂	70	466	8048	0.33 (14.7)	0.88 (39.1)	0.06 (2.7)	0.09 (4.0)	0.05 (2.2)	0.17 (7.6)	0.28 (12.4)	0.34 (15.1)	0.05 (2.2)	-

a) Polymerization condition: [Zr]; 0.005 mmol, MAO; 5 mmol in 250 ml of toluene at 0.1 MPa. Propylene feed; 100 NL/h. Polymerization time; 15 min. (PP1,2,3), 30 min. (PP4,5).
b) kg/mol[Zr]/h. c) GPC data (PP standard). d) estimated by ¹H and ¹³C NMR. e) under 0.01 mol%.

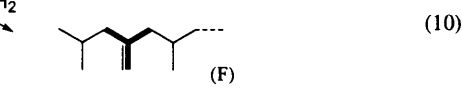
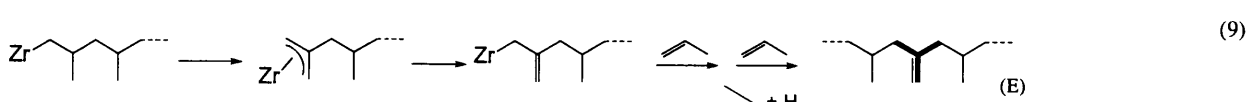
a) 1,2-inserted chain end



b) 2,1-inserted chain end



c) Allylic activation



d) Initiation of monomer insertion

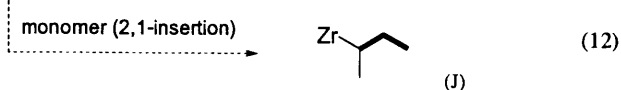
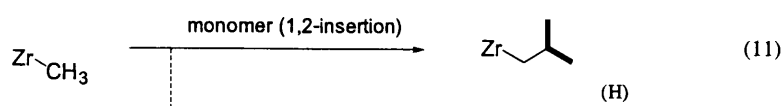


Figure 3-7 Schemes of the possible formation reactions of chain ends

In PP1, n-propyl group (G) was only identified as the saturated chain end structure, and the main unsaturated group at the chain end was vinylidene (A). Based on these results, the following is indicated: in using Cp_2ZrCl_2 , the termination reaction of polymerization was the transfer of a β -hydrogen of the growing polymer chain to a monomer or to the metal center of the catalyst, and that a propylene insertion was a 1,2-insertion predominantly as shown in scheme (1). It corresponds to the result in a previous paper [11].

In PP2 and PP3 that were produced with $\text{En(Ind)}_2\text{ZrCl}_2$, all of structures of (A)-(I) were detected. Among them, vinylidene group (A) and n-propyl group (G) were mainly formed as unsaturated and saturated groups, respectively. Moreover, i-propyl groups (H) and n-butyl groups (I) were identified as having almost the same amounts. Those results would indicate that the reactions as shown in scheme (7) and (11) occurred besides that shown in scheme (1). The presence of 2-butenyl group (C) could be evidence of the chain transfer reaction as shown in scheme (5). Therefore, this would be suggested that termination reaction at 2,1-inserted active chain end occurred. The presence of i-butenyl group (B) and 4-butenyl group (D) could indicate that the isomerization reactions as shown in scheme (4) and (8) occurred. Internal vinylidenes (E, F) would be formed by allylic activations occurring between the metal center of the catalyst and the growing polymer chain.

In PP4 and PP5 that were produced with $\text{iPr(Cp)(Flu)ZrCl}_2$, the formation of vinylidene group (A), i-butenyl group (B) as the unsaturated group and n-propyl group (G), i-propyl group (H) as the saturated group would indicate that the termination reactions occurred at 2,1-inserted active chain end. The presences of 2-butenyl group

(C) and 4-butenyl group (D) could show that the chain end reactions as shown in scheme (5), (6) and (8) occurred at 2,1-inserted chain end. Internal vinylidenes (E, F) would be formed as in PP2 and PP3.

The important point to note here was that total amounts of unsaturated groups were too much compared with the ones of saturated chain end groups. That result could suggest the liberation of hydrogen occurred in polymerization.

In expanded ^{13}C NMR spectra shown in figure 3-8, the signals of i-butenyl group, which appeared between 129 and 133 ppm in PP3 [32], could be hardly observed in PP5. However, different signals that have never been known to the best of our knowledge were observed around 131.7 and 133.9 ppm. As the chemical shifts of those signals would induce a downfield shift from those of i-butenyl group, it would suggest that those signals were assigned as the internal tri-substituted alkenyl group in the polymer chain. In PP4 and PP5, therefore, there would be much internal tri-substituted alkenyl group compared with i-butenyl group.

That structure would be formed via the pathways as shown in figure 3-9. Before the β -hydrogen transfer produces terminal vinylidene group, an allylic activation occurs to form a kind of π -allyl complex between the metal center of the catalyst and the end of growing polymer chain. When it occurs at methyl site near the chain end with liberation of hydrogen, internal vinylidene is generated followed by propylene monomer insertion. When the allylic activation occurs at methylene site, a tri-substituted alkenyl group is generated. Followed by the chain transfer with liberated H_2 , i-butenyl group is formed [26]. On the other hand, followed by propylene monomer insertion, internal tri-substituted alkenyl group appears in the polymer chain. In PP4 and PP5, the latter pathway would occur more easily than the others.

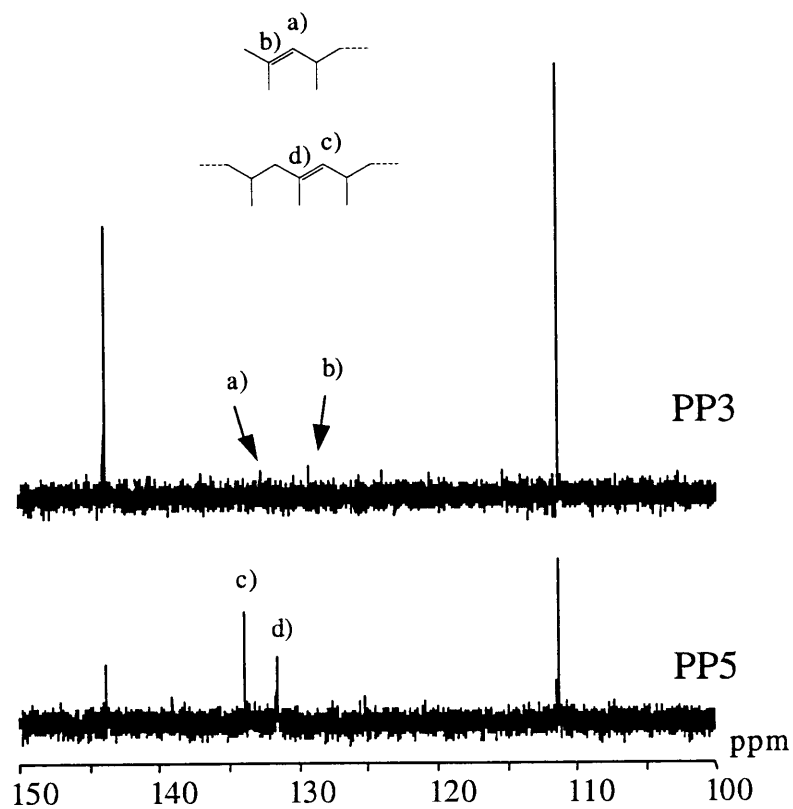


Figure 3-8 Expanded ^{13}C NMR spectra (recorded in Decalin at 118°C) between 100 and 150 ppm of the PP2 and PP5

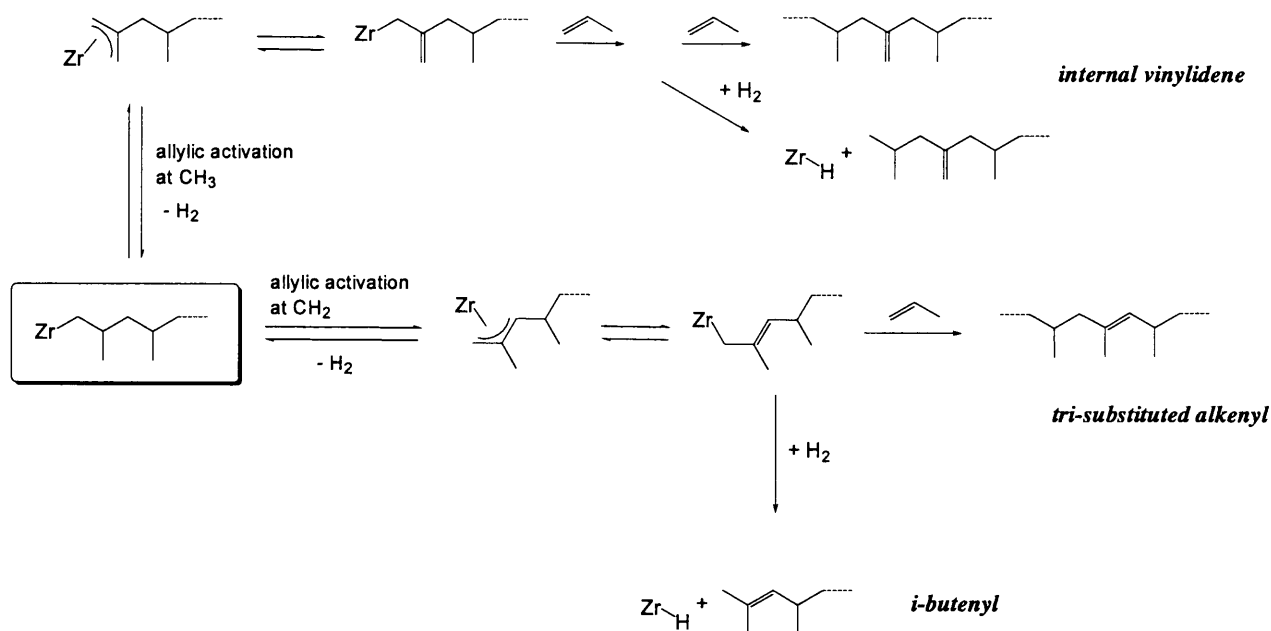


Figure 3-9 Scheme of the proposed mechanism for internal unsaturated groups formation

4. Conclusion

Propylene homopolymerizations were conducted with three kinds of metallocenes to discuss the chain end structures of the polymer and the mechanism of polymerization. In the polymerization with Cp_2ZrCl_2 , the termination reaction exclusively occurred at 1,2-inserted chain end. In cases of $En(Ind)_2ZrCl_2$ and $iPr(Cp)(Flu)ZrCl_2$, besides at 1,2-inserted site, a considerable number of termination reactions occurred at 2,1-inserted chain end. Internal vinylidenes were detected in both metallocenes. Moreover, *i*-butenyl group and internal tri-substituted alkenyl group were identified in $En(Ind)_2ZrCl_2$ and $iPr(Cp)(Flu)ZrCl_2$, respectively. Those structures would be formed via π -allyl complex between the metal center of the catalyst and the growing polymer chain with liberation of hydrogen.

3.3. Unsaturated structures of polyhexene, poly(4-methylpentene) and poly(3-methylpentene) prepared with metallocene catalysts

1. Introduction

It is known generally that metallocene-catalyzed polyolefin possess several unsaturated structures [4, 11-17, 28, 29, 33]. So far, vinyl, butenyl, isobutenyl and internal unsaturated structures have been reported as unsaturated structures in metallocene-catalyzed PP as shown in section 3.1. and 3.2.

One of the other characteristics of metallocene catalysts is that they have good comonomer incorporation for polymerization with narrow molecular weight distribution polymers [11, 13, 34]. Furthermore, they can polymerize the branched bulky olefins compared with previous catalysts. For instance, polyhexene and poly(3-MP-1) have already been synthesized by metallocene catalysts. And, their stereochemistry [35-40] has so far been the subject of study. However, only few studies have reported in previous papers regarding unsaturated structures of those polymers [41, 42] although they are important for industrial usages.

The author aimed to study on the unsaturated structures in polyhexene families, namely, polyhexene, poly(4-MP-1) and poly(3-MP-1), produced with metallocenes, $\text{En}(\text{Ind})_2\text{ZrCl}_2$ and $\text{iPr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$, by ^1H NMR analysis.

2. Experimental section

Materials

Hex-1-ene purchased from Wako Pure Chemical Industries, Ltd. was dried over molecular sieves (4A). 4-Methylpent-1-ene and 3-methylpent-ene monomers (Mitsui

Chemicals) were dried over molecular sieves (4A) before use. Other materials were same as ones in section 3-1 and 3-2. Organometallic compounds were treated under a nitrogen atmosphere.

Polymerization

All polymerization experiments were carried out in 500 ml glass flasks equipped with mechanical stirrer, thermocouple and monomer inlet tube. 250 ml of monomer was added to the reactor. After heating the monomer to 45 °C, MAO in toluene (5 mmol [Al]) was added in the reactor, and then, the polymerization was started by addition of 5 ml of toluene solution dissolved metallocene (0.005 mmol) in the reactor. That temperature was maintained during the polymerization. After that, 5 mL of isobutanol was added to the reactor in order to terminate the polymerization. The reaction mixture was poured in 1 L of methanol. Polymers (H-3, 4, 5) were corrected by filtration and washed with 500 ml of methanol, then dried under reduced pressure at 80 °C for 10 hrs. Polymers (H-1, 2, 6) were separated from methanol by decantation and washed with methanol several times, then dried under reduced pressure at 80 °C for 10 hrs.

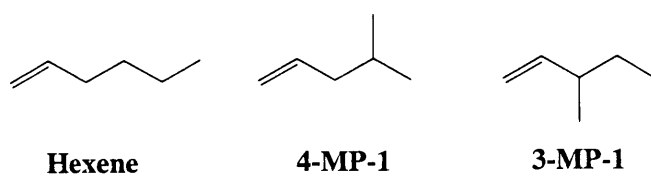
Analysis of polymer

Molecular weights and molecular weight distributions were determined by gel-permeation chromatography (GPC) using o-dichlorobenzene as solvent. ¹H NMR spectra were recorded on a JEOL JNM GSX-400 series in pulse Fourier transform mode. Instrument conditions were as follows: pulse angle, 45 °; pulse repetition, 5.0 sec; spectral width, 8000 Hz; temperature, 120 °C; data points, 32768. Polymer solutions used for NMR were prepared by dissolving 50 mg of polymer sample in 0.5 ml of

1,2-dichlorobenzene- d_4 (ODCB) as solvents.

3. Results and discussion

The author selected three kinds of olefin monomers that were isomers of hexene, namely, hex-1-ene (hexene) as linear monomer, 4-methylpent-1-ene (4-MP-1) and 3-methylpent-1-ene (3-MP-1) as branched ones. And we prepared polyhexene, poly(4-MP-1) and poly(3-MP-1), in monomer liquid pools at same temperature with metallocenes, $\text{En}(\text{Ind})_2\text{ZrCl}_2$ and $\text{iPr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$, chosen as typical ones. It's known that those metallocenes could produce isotactic and syndiotactic polymers, respectively.



Unsaturated structures of the resulting polymers were identified by ^1H NMR with ODCB as a solvent to restrain the isomerization during the measurement [31]. Expanded ^1H NMR spectra of the resulting polymers are shown in figures 3-10. On the basis of the previous papers describing the assignment of ^1H NMR spectra [4, 11, 14, 17, 29], several types of unsaturated structures would be observed in resulting polymers; vinylidene, $\text{CH}_2=\text{CRR}'$, (Vd; between 4.7 and 4.8 ppm), vinyl, $\text{CH}_2=\text{CHR}$, (Vn; 4.9 and 5.7 ppm), tri-substituted vinylene, $\text{RCH}=\text{CR}'\text{R}''$, (3Vn; 5.2 ppm) and di-substituted vinylene, $\text{RCH}=\text{CHR}'$, (2Vn; between 5.3 and 5.5 ppm). The results of polymerization and the data of identified unsaturated structures are summarized in table 3-2.

Table 3-2 Results of polymerization^{a)} with metallocene catalysts

Run#	Monomer	Metallocene	Activity (Kg/mmol[M]/h)	M_w^b (g/mol)	M_w/M_n	Unsaturated groups in polymer (unit mol%) ^{c)} In brackets, percentages of units in unsaturated structures			
						2Vn (RCH=CHR')	Vd (CH ₂ =CRR')	3Vn (RCH=CR'R'')	Vn (CH ₂ =CHR)
H-1	Hexane	En(Ind) ₂ ZrCl ₂	32448	29500	1.94	0.54 (95)	0.03 (5)	-	-
H-2	Hexane	iPr(Cp)(Flu)ZrCl ₂	35808	48400	1.80	0.45 (97)	0.01 (3)	-	-
H-3	4-MP-1	En(Ind) ₂ ZrCl ₂	4004	25000	1.81	0.60 (79)	0.04 (5)	0.12 (16)	-
H-4	4-MP-1	iPr(Cp)(Flu)ZrCl ₂	697	34000	1.85	0.64 (80)	0.02 (2)	0.14 (18)	-
H-5	3-MP-1	En(Ind) ₂ ZrCl ₂	955	41000	2.51	-	0.19 (46)	0.19 (46)	0.03 (8)
H-6	3-MP-1	iPr(Cp)(Flu)ZrCl ₂	37	3150	2.14	-	0.61 (16)	2.72 (74)	0.38 (10)

a) Polymerization condition: [Zr]; 0.005 mmol, MAO; 5 mmol in 250 ml of monomer liquid pool. Propylene feed; 100 NL/h. Polymerization time; 15 min. (H-1,2,3,4), 60 min. (H-5,6). b) GPC data (PS standard). c) estimated by ¹H NMR.

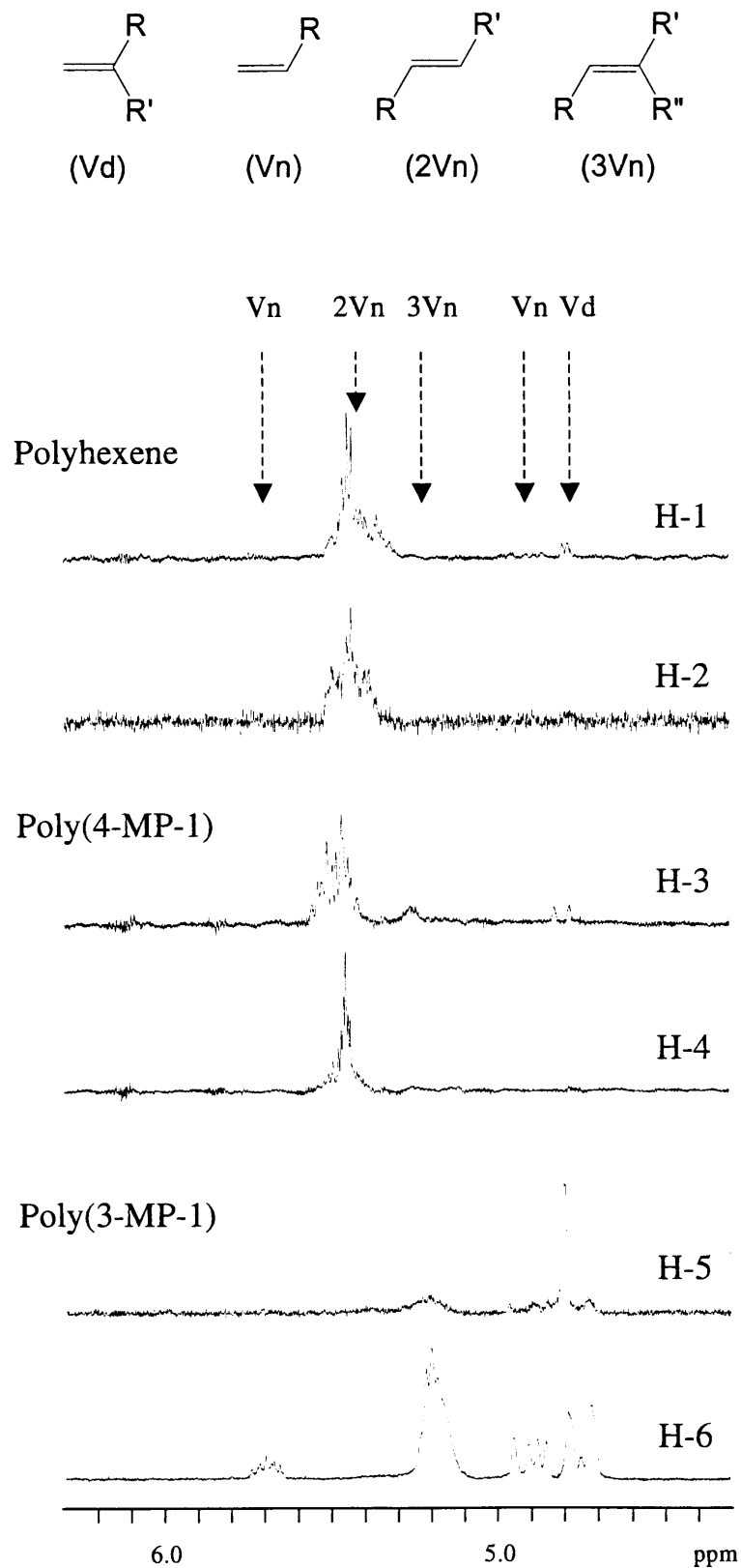


Figure 3-10 Expanded ^1H NMR of the olefinic region of resulting polymers

In polyhexene, which were H-1 and H-2, di-substituted vinylene structure (2Vn) was identified as the main unsaturated structure, and a small amount of vinylidene one (Vd) was also observed. In case of poly(4-MP-1), H-3 and H-4, di-substituted vinylene structure (2Vn) was identified as the main unsaturated one, and a small amount of vinylidene one (Vd) was formed in both polymers. Furthermore, tri-substituted vinylene structure (3Vn) was observed in both polymers. In poly(3-MP-1), H-5 and H-6, a tri-substituted vinylene structure (3Vn) was formed mainly. Vinylidene one (Vd) was identified at some level. Moreover, vinyl structure (Vn) was formed in both polymers.

Unsaturated structures in polyolefin, in general, would be formed by termination reaction of a polymerization. Based on previous papers [4, 11, 14-17, 29, 31, 33], schemes of possible formation reactions of unsaturated structures might be indicated as figure 2. According with that assumption shown in those schemes, the followings would be suggested; (a) the termination reaction of polymerization of hexene mainly occurred at the 2,1-inserted active chain end by the elimination of a β -hydrogen of the growing polymer chain to a monomer or to the metal center of the catalyst as shown in Scheme (4). (b) In 4-MP-1 polymerization, the reactions at the 1,2-inserted active chain end as shown in Scheme (1) and (2) occurred at some level besides at the 2,1-inserted active chain end shown in scheme (1). (c) In case of 3-MP-1 polymerization, the termination reaction occurred at the 1,2-inserted active chain end by the elimination of a β -hydrogen or a β -alkyl group as in Figure 3-11 (1), (2) and (3).

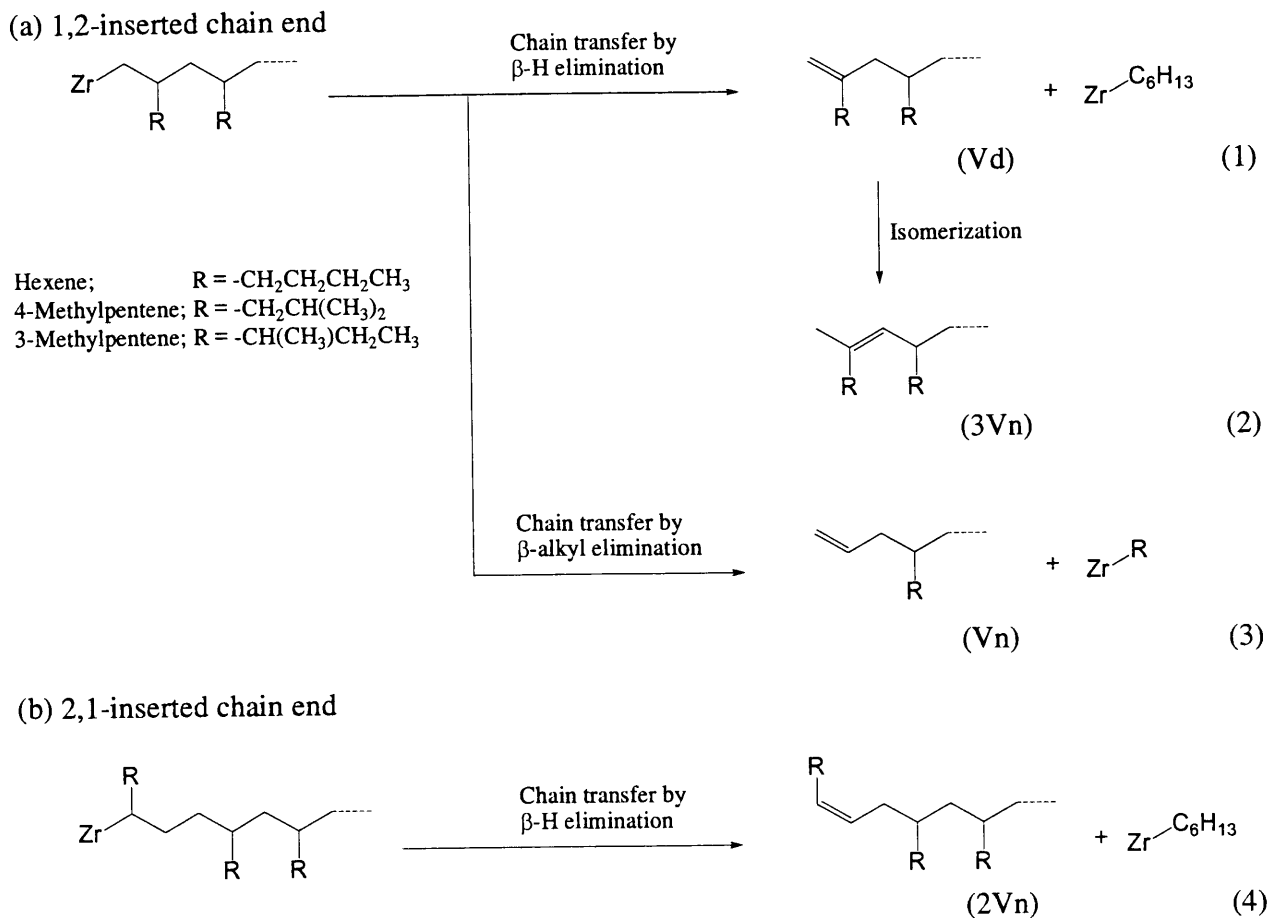


Figure 3-11 Schemes of the possible formation reactions of unsaturated structures at the polymer chain end

In here, the remarkable differences were not observed in metallocenes, $\text{En}(\text{Ind})_2\text{ZrCl}_2$ and $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$. Therefore, the differences of unsaturated structures among the resulting polymers could be attributed to an interaction between the branched methyl group of monomers and metallocene catalysts more than an influence of metallocene structures. In further investigation of detailed unsaturated structures of polymers, we should consider the isomerization by a chain working [42] and the internal unsaturated one by an allylic activation [31].

4. Conclusion

Hexene, 4-MP-1 and 3-MP-1, homopolymerizations were conducted with metallocenes: $\text{En}(\text{Ind})_2\text{ZrCl}_2$ and $\text{iPr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$. ^1H NMR analyses of the resulting polymers were carried out to identify the unsaturated structures of those polymers. In polyhexene and poly(4-MP-1), the di-substituted vinylene structure (2Vn) was mainly observed. On the other hand, in poly(3-MP-1), the tri-substituted vinylene (3Vn), vinylidene (Vd) and vinyl (Vn) structures were identified for the first time.

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Chapter 4

New methodology for synthesizing polyolefinic graft block copolymers and their morphological features

1. Introduction

Nowadays, a considerable amount of polyolefins is used for the molded products after blending two or more kinds of polyolefins, because polyolefin blends bring about unique and improved properties. Generally speaking, block copolymers play important roles in compatibilizing the blended polymers. Therefore, polyolefinic block copolymers are expected to compatibilize different kinds of polyolefins that are naturally immiscible combinations. Such effort will be able to create new class of plastic materials from polyolefins that are regarded as commodities so far. The polyolefinic block copolymers are classified into two types that are linear and graft types. Until now, two and one methodologies have been reported for synthesizing the former and the latter, respectively.

To synthesize the former, living polymerization of olefins has been intensively studied and many useful catalysts have been discovered [1-7]. These catalysts enabled us to observe the well-defined morphologies of linear block copolymers with TEM [8, 9]. Alternative method for producing linear polyolefinic block copolymers is use of bis(2-aryindenyl) metallocenes to obtain stereoblock PP [10] and its morphological change during and after tensile extension was observed [11]. To synthesize the latter, copolymerization of macromonomers with olefins has been investigated [12, 13].

Needless to say, the variety of the segments in the block copolymers is limited in the field of applicability of each method. Then, new methodology for synthesizing polyolefinic block copolymers is desired to diversify the combinations of the components in polyolefinic block copolymers. Therefore, the author investigated a new route to graft polyolefinic block copolymers with polymer coupling reaction as an application of our expertise in synthesizing terminally hydroxylated PP (PP-OH) [14].

Suitable partners for PP-OH in coupling reaction would be maleic anhydride modified polyolefins that are conventional resins and expected to show high reactivity to hydroxyl group of PP-OH [15]. In this study, the author introduces coupling reaction of PP-OH with maleic anhydride modified polyethylene (PE-*g*-MAH) and maleic anhydride modified ethylene-propylene random copolymer (EPR-*g*-MAH).

2. Experimental section

Materials

Diisobutylaluminiumhydride (DIBAL-H) was purchased from Tosoh Finechem Co. and used as received. Decane (Mitsui Chemicals Fine, Inc.) was dried over CaCl₂ before use. *p*-toluenesulfonic acid was purchased from Wako Pure Chemical Industries, Ltd.. Pyrolysis PP (py-PP) obtained in the conventional way [16] was used for hydroxylation to synthesize PP-OH. Its weight average molecular weight (M_w) was 8,000 and its molecular weight distribution (M_w/M_n) was 2.4. It was isotactic PP copolymerized with 2 mol% of ethylene. PE-*g*-MAH and EPR-*g*-MAH that were obtained in the conventional way [17] were used for coupling reaction with PP-OH. The values of M_w of PE-*g*-MAH and EPR-*g*-MAH were 45,000 and 130,000, respectively. The M_w/M_n values of PE-*g*-MAH and EPR-*g*-MAH were 2.4 and 2.0, respectively. PE was homopolyethylene and EPR consisted of 81 mol% of ethylene and 19 mol% of propylene. The contents of MAH in PE-*g*-MAH and EPR-*g*-MAH were 1.8 wt% and 1.0 wt%, respectively.

Hydroxylation

Into a nitrogen-purged 1 L glass reactor equipped with a mechanical stirrer, 26.6 g of

py-PP was added with 34.6 mmol of DIBAL-H and 800 mL of *n*-decane. It was heated to 100 °C and that temperature was maintained for 7 h with stirring. Then, dried air was fed into it at a rate of 200 L/h at that temperature for 6 h. The resulting solution was poured into a mixture of 2 L of methanol, 2 L of acetone and small amount of HCl, followed by string with a magnetic stirrer chip for 2 h. Thus-obtained polymer (PP-OH) was recovered by filtration, washed with 1 L of methanol, and dried at 80 °C for 5 h.

Coupling reaction

Into a nitrogen-purged 400 mL glass reactor equipped with a mechanical stirrer, 1.25 or 1.0 g of PP-OH was added with 150 mL of decane, catalyst amount of *p*-toluenesulfonic acid and 1.75 g of PE-*g*-MAH or 2.8 g of EPR-*g*-MAH, respectively. It was heated to 80 or 140 °C, respectively, and the temperature was maintained for 8 or 7 h with stirring. Then, it was poured into a mixture of 1.5 L of methanol and 1.5 L of acetone, followed by stirring with a magnetic stirrer chip for 5 min. The recovered polymer by filtration was stirred in 2 L of acetone with a magnetic stirrer chip for 2 h. Thus-obtained polymer was recovered by filtration, washed with 0.5 L of acetone, and vacuum-dried at 80 °C for 10 h.

Polymer blend

For comparison with graft polyolefinic block copolymers, same procedures as described in Coupling Reaction except for using py-PP instead of PP-OH were carried out to prepare polymer blends.

Analysis

Molecular weights of a graft polyolefinic block copolymer and a polymer blend were measured by a Millipore Waters 150C gel permeation chromatography (GPC) equipped with a refractive index detector, using polyethylene calibration. Morphologies of graft polyolefinic block copolymers and polymer blends were observed with TEM as following. Ultra-thin (ca. 100 nm) section of the polymer that had been pressed to give a sheet and dyed with RuO₄ was prepared with a Reica Ultracut microtome equipped with a diamond knife at -100 °C. The specimen was examined with a HITACHI H-810 transmission electron microscopy operated at 100 KV at 10,000 and 150,000 magnifications. The analysis with ¹³C NMR was performed in the same manner as our previous paper [14]. Solubilities of a graft polyolefinic block copolymer and a polymer blend to decane at 23 °C (C10 Sol) were measured as following. Into a 1 L flask, 1 g of the polymer sample was added with 10 mg of 2,6-di-*t*-butyl-4-methylphenol and 500 mL of decane. The mixture was heated to 150 °C in order to dissolve the polymer sample. The obtained solution was cooled to 23 °C during 8 h and kept at that temperature for 8 h. The resulting slurry was filtered and the liquid phase portion was vacuum-dried until it reached constant weight. The percentage of thus-obtained constant weight in the weight of the initial polymer sample was C10 Sol.

3. Results and discussion

Hydroxylation of py-PP

Chain-end structures of py-PP were investigated with ¹³C NMR and the major group was vinylidene group as shown in table1, which is accordance with the literature on pyrolysis of PP [18]. It was used for preparing PP-OH through hydroalumination with

DIBAL-H, oxidation with dried air and methanolysis. The chain-end structures of the resulting polymer were analyzed with ^{13}C NMR and summarized in Table 4-1 in comparison with those of py-PP. The formation of 45 mol% of hydroxyl chain-end group from the vinylidene group accounting for 81 mol% in py-PP means comparable conversion with that observed in the hydroxylation of high molecular weight PP possessing alkylaluminum at its chain end [14]. Consequently, the obtained polymer possessed hydroxyl chain end in the content of 45 mol% of both ends of the polymer chain, namely, 0.9 hydroxyl group per chain on the average, although it would be a mixture of di-hydroxylated, mono-hydroxylated and non-hydroxylated polymers.

Table 4-1 The proportions of chain-end groups of pyrolysis and hydroxylated PP.

Sample	Chain-end group ^{a)} / mol%				
	Vd	<i>n</i> Pr	<i>i</i> Pr	<i>i</i> Pr-OH	Others
py-PP	81	17	2	n.d. ^{b)}	n.d.
PP-OH	6	15	34	45	n.d.

^{a)} Vd: vinylidene; *n*Pr: *n*-propyl; *i*Pr: *i*-propyl; *i*Pr-OH: hydroxy *i*-propyl.

^{b)} Not detected.

Coupling reaction between PP-OH and PE-g-MAH

Thus-obtained PP-OH was reacted with PE-g-MAH at 80 °C for 8 h in decane with a molar ratio of 4 to 1 to synthesize PE-g-PP. This kind of coupling reaction between polyolefins has never been reported so far to the best of our knowledge, although coupling reaction between a maleic anhydride modified polyolefin and a polar polymer such as polyamide has been known well [19]. For its comparison, py-PP was blended with PE-g-MAH under the same conditions as the coupling reaction expect for the replacement of PP-OH by py-PP. Then, the both were compared with GPC analysis. As shown in figure 4-1, a peak in low molecular weight region of PE-g-PP is obviously smaller than that of the polymer blend and, in its place, PE-g-PP has the larger peak in high molecular weight region. They would clearly show that PP-OH forming the peak in low molecular weight region was bonded to PE-g-MAH by the reaction between -OH and -MAH units.

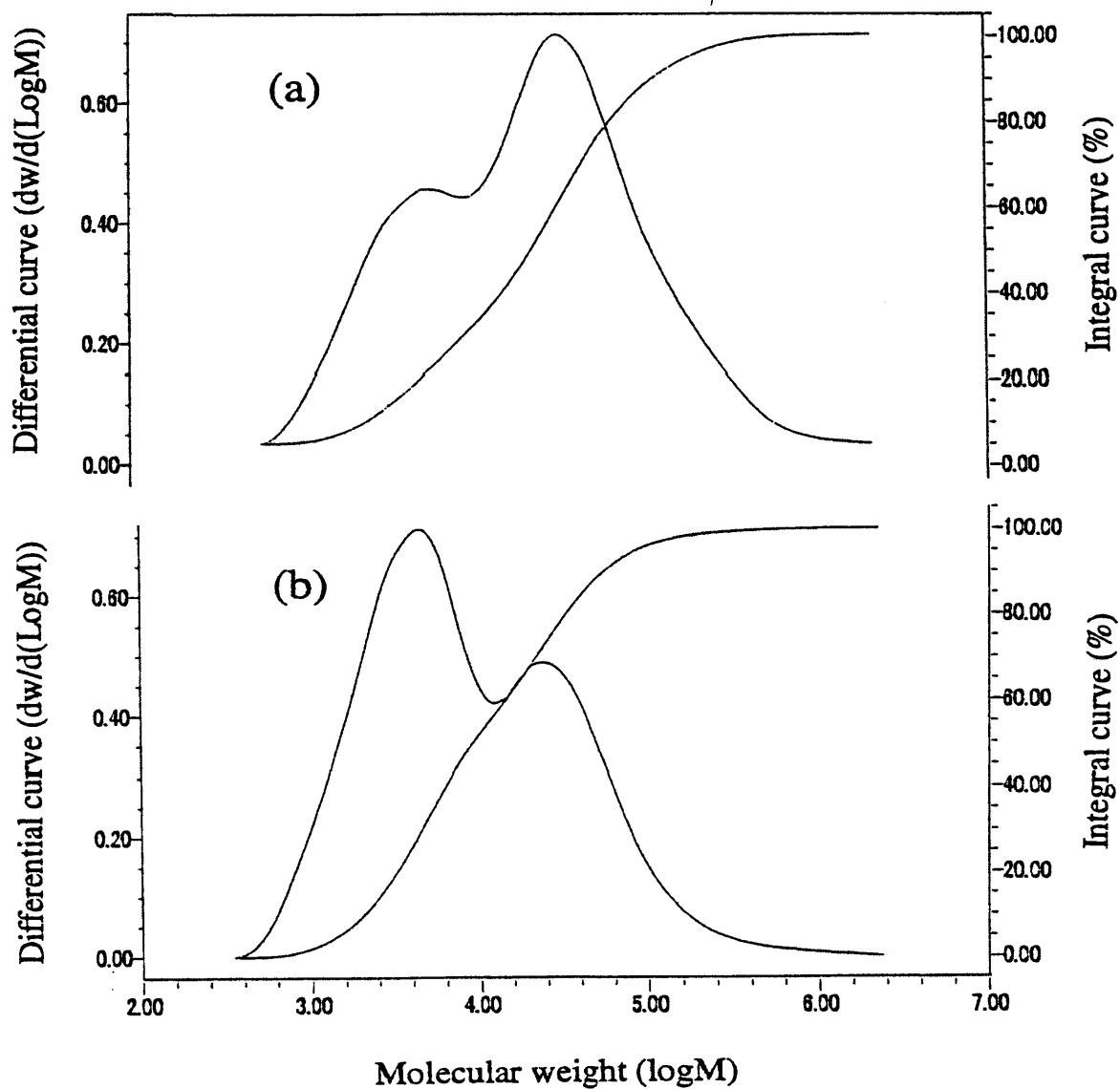


Figure 4-1 GPC diagrams of (a) PE-*g*-PP produced by coupling reaction between PP-OH and PE-*g*-MAH and (b) polymer blend consisting of py-PP and PE-*g*-MAH. The molar ratio of PP segment to PE segment is 4 to 1 in any of the both.

Next, the both were compared in observation with TEM. The both showed phase separation morphology where the matrix was PE segment and the dispersed phase was PP segment as in figure 4-2. Evidently, the size of the dispersed phase in PE-*g*-PP was much smaller than that in the polymer blend. Although the peak in low molecular weight region of PE-*g*-PP in figure 4-1 means presence of PP-OH unreacted with PE-*g*-MAH, there were no coarse dispersed domains as shown in figure 4-2 (a). It indicates that the formed PE-*g*-PP acted as a compatibilizer between unreacted PP-OH and PE segment.

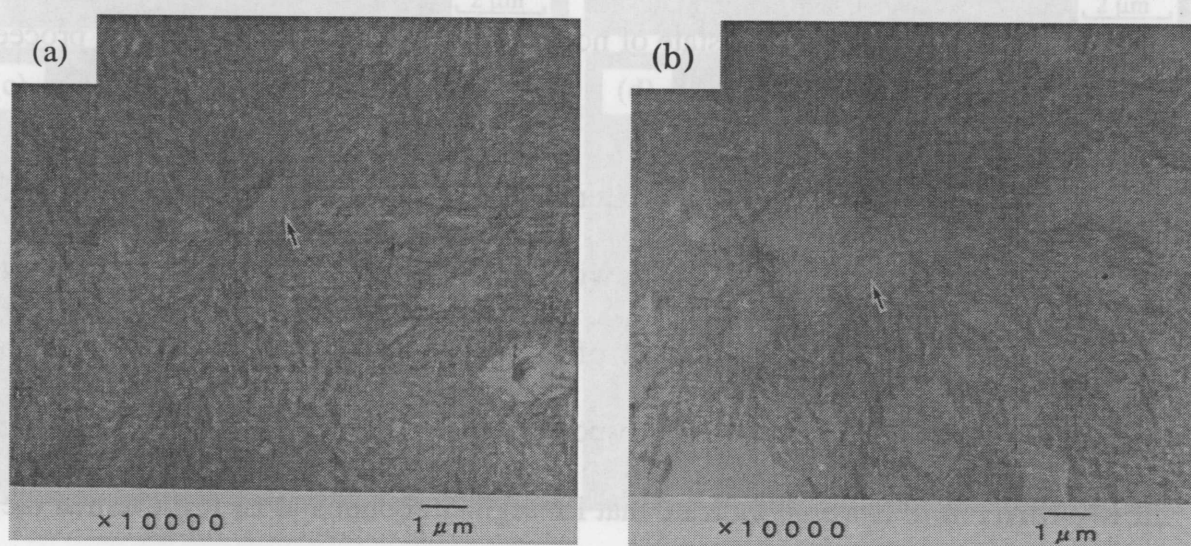


Figure 4-2 TEM micrographs at 10,000 magnification from (a) PE-*g*-PP produced by coupling reaction between PP-OH and PE-*g*-MAH and (b) polymer blend consisting of py-PP and PE-*g*-MAH. The molar ratio of PP segment to PE segment is 4 to 1 in any of the both.

Coupling reaction between PP-OH and EPR-g-MAH

Alternatively, studies on combination of crystalline polyolefins and amorphous polyolefins are of importance to create new class of plastic materials. As an example, PP-OH was reacted with EPR-g-MAH at 140 °C for 7 h in decane with a molar ratio of 6 to 1 to synthesize EPR-g-PP. For its comparison, py-PP was blended with EPR-g-MAH under the same conditions as the coupling reaction expect for the replacement of PP-OH by py-PP. In the coupling reaction, its non-viscous initial solution changed to jelly-like product through highly viscous solution, although that in blending the polymers kept the state of non-viscous solution. It suggests the proceeding of the aimed coupling reaction.

Each product was poured into a mixture of methanol and acetone, then, the polymer recovered by filtration was washed with acetone followed by vacuum dry to be compared in C10 Sol. The C10 Sol. of EPR-g-PP was 8.8 wt%, while that of the polymer blend was 75.3 wt% corresponding nearly to the weight proposition of EPR-g-MAH in it. It would indicate that PP segment bonded to EPR prevented the EPR segment from dissolving in decane.

Figure 4-3 shows morphologies observed with TEM for press sheets from the respective polymers. Phase separation morphology was observed in the polymer blend, where the matrix was EPR segment and the dispersed phase was PP segment (figure 4-3 (b)). It was common morphology for polyolefins as done in figure 2 and the dispersed phase was found to be considerably large and non-uniform. On the contrary, EPR-g-PP demonstrated unique lamella microstructure as shown in figure 4-3 (a). Furthermore, its phase boundary was not distinct at high magnification as seen in figure 4-3 (c), although the phase boundary was clear in the polymer blend even at high magnification (figure

4-3 (d)).

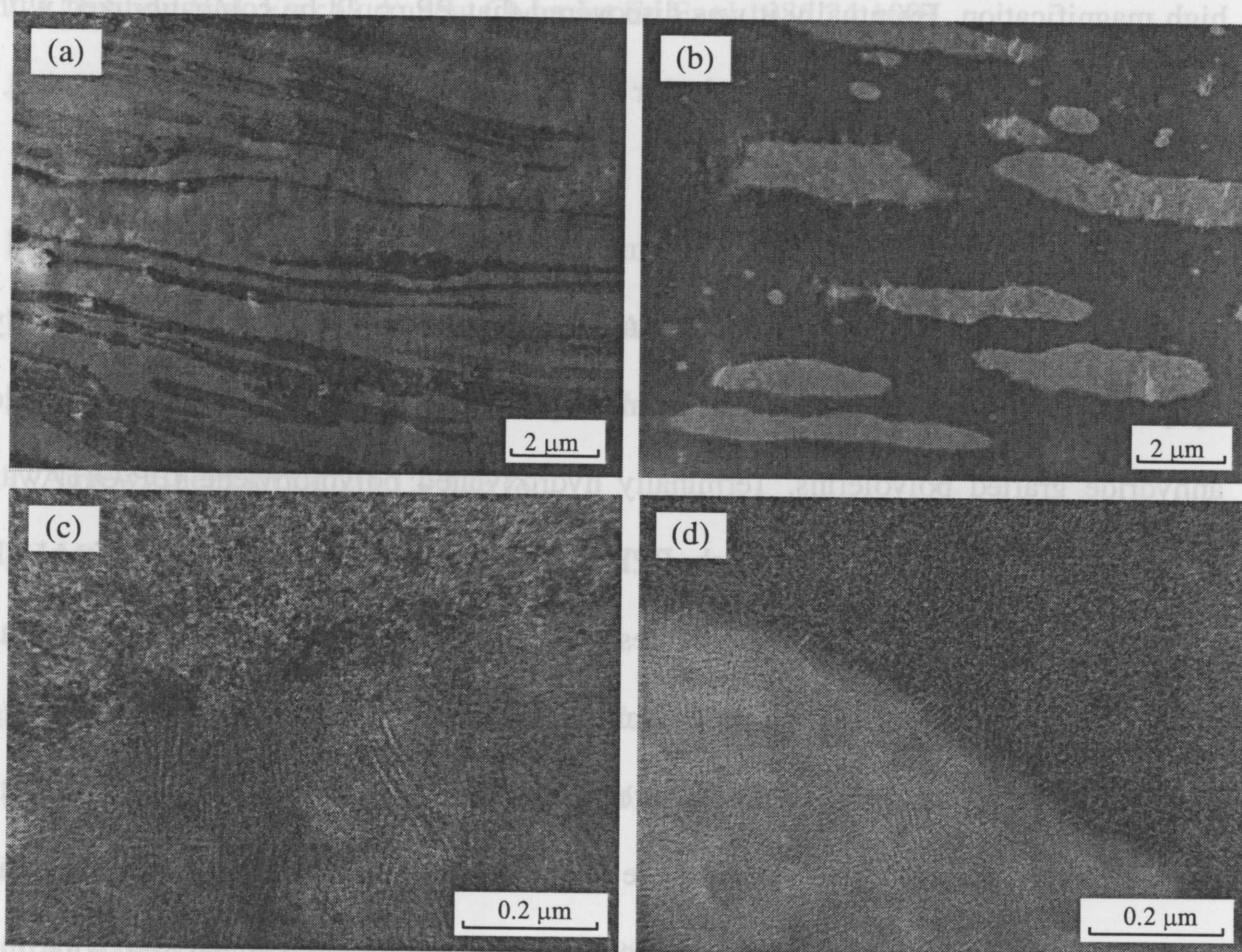


Figure 4-3 TEM micrographs at 10,000 magnification from (a) EPR-g-PP produced by coupling reaction between PP-OH and EPR-g-MAH and (b) polymer blend consisting of py-PP and EPR-g-MAH and at 150,000 magnification of (c) the EPR-g-PP and (d) the polymer blend. The molar ratio of PP segment to EPR segment is 6 to 1 in any of the both samples.

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[17] Yamanaka T, Miura E. Japanese Laid Open Patent 4-57808.

[18] Sawaguchi T, Ikemura T, Seno M. *Macromolecules* 1995;28:7973.

Namely, the lamellar domains looked black or white at low magnification were turned out to include the other component on a nano-order scale by the observation at high magnification. Eventually it was discovered that PP could be compatibilized with EPR completely to give the novel polymer phase morphology by this coupling reaction.

4. Conclusion

This study describes a new synthetic route for polyolefinic graft block copolymers by adopting coupling reaction between terminally hydroxylated polyolefins and maleic anhydride grafted polyolefins. Terminally hydroxylated polypropylene (PP-OH) was coupled with PE-*g*-MAH and such EPR-*g*-MAH to give polyolefinic graft block copolymers (PE-*g*-PP and EPR-*g*-PP, respectively). The formation of PE-*g*-PP was confirmed by enhancement on molecular weight compared with the corresponding polymer blend. It brought about distinctively decrease in size of dispersed domain in its phase separation morphology. Occurrence of coupling reaction to give EPR-*g*-PP was indicated by extreme decrease in its solubility to decane in comparison with the corresponding polymer blend. It led to unique morphology demonstrating lamella microstructure that had never been reported for a comparable polyolefin composite.

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Chapter 5

Synthetic method of polyethylene-poly(methylmethacrylate)

**(PE-PMMA) polymer hybrid via reversible
addition-fragmentation chain transfer (RAFT)
polymerization with functionalized polyethylene**

1. Introduction

Recent advances in polyolefin chemistry have led to the creation of polymer hybrid linking between polyolefins and polar polymer segments by combination between functionalized polyolefins and several processes such as radical, anionic, cationic polymerizations and post polymerization reactions, bringing the ordinary polyolefins some improved and unique properties to broaden the applications of polyolefins to highly profitable fields [1-5].

Allowing for the production of polymer hybrid based on polyolefins, in the early stage, irradiated polyolefin was used as an initiator for radical polymerization [6, 7]. That method, however, was difficult to control the graft density and the side chain length of polar polymer segments. In recent years, several studies have been reported by using control radical polymerization (CRP) methods [8-14]. CRP would be attractive tools because of the controllability of polymerization, and they would be expected as versatile methods to synthesis of well-defined polymer hybrids. However, the atom transfer radical polymerization (ATRP) [8-12], which is a transition metal mediated radical polymerization, is adopted in many cases of them, and removal step of the catalyst ash is needed for purification of resulting polymer in case of ATRP. Moreover, other CRP methods have hardly been studied to produce polymer hybrid based on polyolefins.

In previous studies of reversible addition-fragmentation chain transfer (RAFT) polymerization, which is a metal free CRP method [17-21], several polymer hybrids based on polystyrene, cellulose, FEP film and silica surface, have already been reported [13-16]. The author's motivation in here was to apply the RAFT polymerization method to synthesize polymer hybrids based on polyolefins. At first, the author synthesized the

PE chain transfer agent (PE-CTA) possessing the dithiobenzoate group obtained by sequential functionalization of terminally hydroxylated PE. Then, PE-PMMA polymer hybrids were produced via RAFT polymerization.

2. Experimental section

Materials

Dimethylsilylene(2,7-tert-butyl-fluorenyl)(2-methyl-benz[e]indenyl)zirconium dichloride was prepared according with previous paper [22]. Methylaluminoxane (MAO) purchased from Albemarle Co. was dried under vacuum and diluted in toluene. Allyl alcohol was purchased from Tokyo Kasei Kogyo Co., Ltd. and purified by distillation. Triisobutylaluminum (TIBAL) was purchased from Tosoh Finechem Co. and used as received. Toluene purchased from Wako Pure Chemical Industries, Ltd. was dried over sodium metal and distilled before use. Tetrahydrofuran (THF) purchased from Wako Pure Chemical Industries, Ltd. was dried over sodium/potassium alloy and distilled before use. Ethylene monomer (Mitsui Chemicals) was used without any further purification. 2-Chloro-2-phenylacetyl chloride was purchased from Wako Pure Chemical Industries, Ltd. and used as received. Triethylamine and carbon disulfide purchased from Wako Pure Chemical Industries, Ltd. were dried over molecular sieves (4A) before use. Phenyl magnesium chloride THF solution was purchased from Kanto Kagaku, Ltd. and used as received. Methylmethacrylate (MMA) was purchased from Wako Pure Chemical Industries, Ltd. and purified by distillation. Organometallic compounds were treated under the nitrogen atmosphere.

Analysis

^1H NMR spectra were recorded on a JEOL JNM GSX400 spectrometer (400 MHz) with TCE or ODCB as solvents at 120 °C. The molecular weights (M_w and M_n) of the polymers were determined at 145 °C with Waters Alliance GPC2000 equipped with four TSKgel columns (two TSKgel GMH6HT columns and two TSKgel GMH6-HTL columns) calibrated with PE. *o*-Dichlorobenzene was used as a solvent at a flow rate of 1.0 mL/min.. IR spectra were recorded on a JEOL FT-IR 410 spectrometer. TEM Analysis was carried out with ultrathin (ca. 100 nm) sections of the polymer were cut on a Reica Ultracut microtome equipped with a diamond knife at a low temperature and then were stained with RuO_4 . TEM observations were made with a Hitachi H-7000 transmission electron microscope at an acceleration voltage of 75 kV.

Preparation of terminally hydroxylated PE (PE-OH)

Polymerization was carried out in 2 L of glass flasks equipped with mechanical stirrer, thermocouples and monomer inlet tube. Into the reactor, 1700 mL of toluene was introduced. After heating the solvent to 45 °C, TEAL (96 mmol) and allyl alcohol (80 mmol) was added. Then, dimethylsilylene(2,7-tert-butyl-fluorenyl)(2-methyl-benz[e]indenyl)zirconium dichloride (0.05 mmol) activated by MAO in toluene solution (3.5 mmol as Al atom) was added into the reactor. The polymerization was started by introduction of ethylene gas. Polymerization temperature was kept at 50 °C under the constant ethylene feed, 10 NL/h. After 3 hour, 20 mL of isobutanol was added to the reactor in order to terminate the polymerization. The reaction mixture was poured in 3 L of methanol. Resulting polymer was obtained by filtration and washed with methanol, then dried under the

reduced pressure at 80 °C for 10 hour. 25.6 g of polymer was obtained. Molecular weights were as follows; $M_w = 36,600$, $M_n = 13,600$, $M_w/M_n = 2.69$. The content of hydroxyl group in polymer was 0.16 mol% (The estimated hydroxyl group content is 0.8 unit [-OH] per polymer chain).

Preparation of polyethylene-chloro(phenyl)acrylate (PE-CPA)

PE-OH (30.95 g; 1.75 mmol [OH]) was dissolved in toluene (250 mL) at 110 °C, and then it was cooled to 80 °C. Triethylamine (11 mL, 80 mmol) and 2-Chloro-2-phenylacetyl chloride (4.5 mL, 27 mmol) were added to the solution at that temperature. The reaction mixture was stirred at 80 °C for 4 hour. It was poured into 1 L of acetone. Obtained polymer was washed with methanol (1 L) and acetone (1 L), then, it was dried under vacuum at 50 °C for 10 hour. 29.65 g of polymer (PE-CPA) was obtained.

$^1\text{H NMR}$ ($\text{C}_2\text{D}_2\text{Cl}_4$), δ 0.85-1.80 (-CH₂- or CH₃ of PE), 3.80-4.20 (*m*, 2H, -CH₂-O-), 5.31 (*s*, 1H, -CH(Ph)Cl), 7.25-7.65 (*m*, 5H, Ar).

FTIR, (KBr): 1760 (C=O), 1155 cm⁻¹ (C-O-C).

Preparation of polyethylene-carbonylphenylmethyl dithiobenzoate (PE-CPDB)

Phenyl magnesium chloride in THF (2M; 10 mmol) was transferred in a dried Schlenk flask. THF (25 mL) and carbon disulfide (41.6 mmol) was added to dropwise to the flask over 10 minute, and the solution temperature was then raised to 40 °C, forming a brown solution. The solution was transferred to another Schlenk flask containing PE-CPA (15.0 g) and THF (120 mL). The reaction mixture was stirred at 60 °C for 26 hour. It was poured into 1 L of acetone. Obtained polymer was washed with methanol (1

L) and acetone (1 L), then, it was dried under vacuum at 50 °C for 10 hour. 15.1 g of polymer (PE-CPDB) was obtained. It was used as PE-CTA.

^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$), δ 0.85-1.80 (-CH₂- or CH₃ of PE), 3.80-4.20 (*m*, -CH₂-O-), 5.30 (*s*, -CH(Ph)Cl), 7.20-7.70 (*m*, 10H, Ar), 8.12 (*d*, -SC(Ar-H)(=S)).

FTIR, (KBr): 1760 (C=O), 1155 cm⁻¹ (C-O-C).

Polymerization of MMA using PE-CPDB

A typical polymerization process is as follows: after PE-CPDB (3.14 g) was placed in a 100 mL Schlenk flask equipped with a stirring bar, toluene (15 mL), MMA (10.7 mL; 100 mmol) and a solution of AIBN (3.0 mg, 0.02 mmol) in toluene was added and the mixture was heated at 60 °C for 24 hour. After cooling, the reaction mixture was poured into 400 ml of methanol and the white solid was collected by filtration. The obtained polymers were purified with boiling THF by Soxhlet extractor for 16 hour, and dried at 50 °C in vacuum for 20 hour.

3. Results and discussion

Preparation of PE-CTA

The synthesis of PE-CTA involved three steps (figure 5-1).

In the first step, PE-OH, which possessed primary alcohol at its chain end, was successfully obtained through the copolymerization of ethylene with aluminum-protected allyl alcohol with our proprietary metallocene catalyst system [22]. In the second step, the terminally hydroxyl group of PE was reacted with 2-chlorophenylacetylchloride to produce PE-CPA. The reaction was performed under a solution condition at 80 °C through the addition of excess 2-chlorophenylacetylchloride

and triethylamine to yield sufficient reactivity of the terminal hydroxyl group enclosed by crystalline PE. In the third step, the PE-CPA was reacted with dithiocarbonyl compound to produce the PE-CPDB, which could be used as a chain transfer reagent (PE-CTA) for RAFT polymerization. The reaction was carried out below 80 °C to prevent the decomposition of the resulting compound.

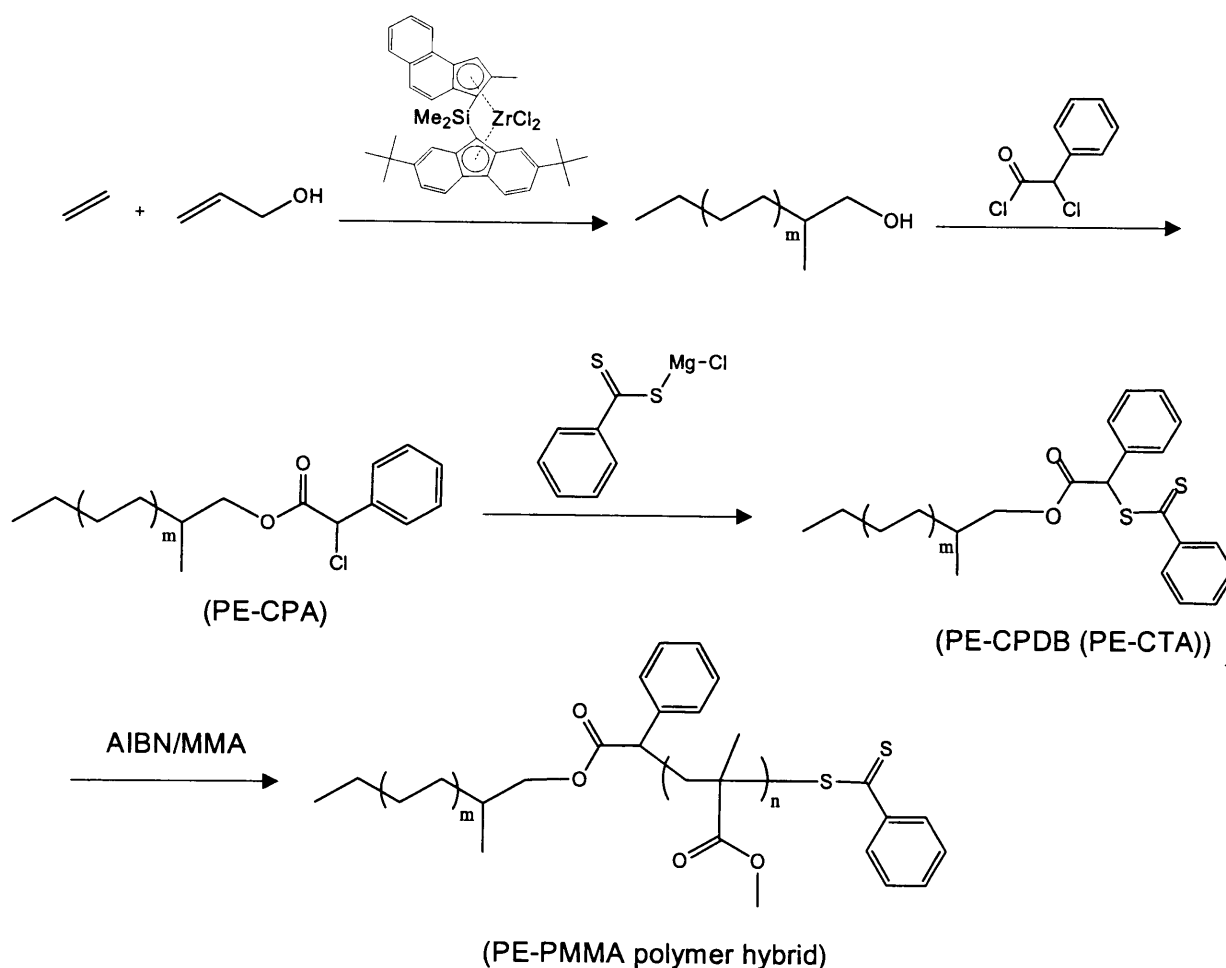


Figure 5-1 Synthetic route for PE-PMMA polymer hybrid via RAFT polymerization method

Figure 5-2 shows the ^1H NMR spectra of PE-OH, PE-CPA and PE-CPDB. The multiple peaks of 3.2-3.4 ppm are assigned to methylene ($-\text{CH}_2\text{-OH}$) at the terminal. From ^1H NMR analysis, 80 % of chain end of the polyethylene was hydroxyl group. For PE-CPA, the multiple peaks of 3.8-4.2 ppm correspond to methylene ($-\text{CH}_2\text{-O-}$), and the single peak of 5.3 ppm corresponds to methine ($-\text{CH}(\text{Ph})\text{Cl}$). The multiple peaks of 6.9-7.5 ppm correspond to phenyl group; no peaks of methylene ($-\text{CH}_2\text{-OH}$) are evident, and this indicates the presence of PE-CPA and the absence of unreacted hydroxyl group. For PE-CPDB, almost of all peaks are similar as PE-CPA except the multi peaks around 8.1 ppm. These would be assigned to two protons of phenyl group nearby dithiocarbonyl group.

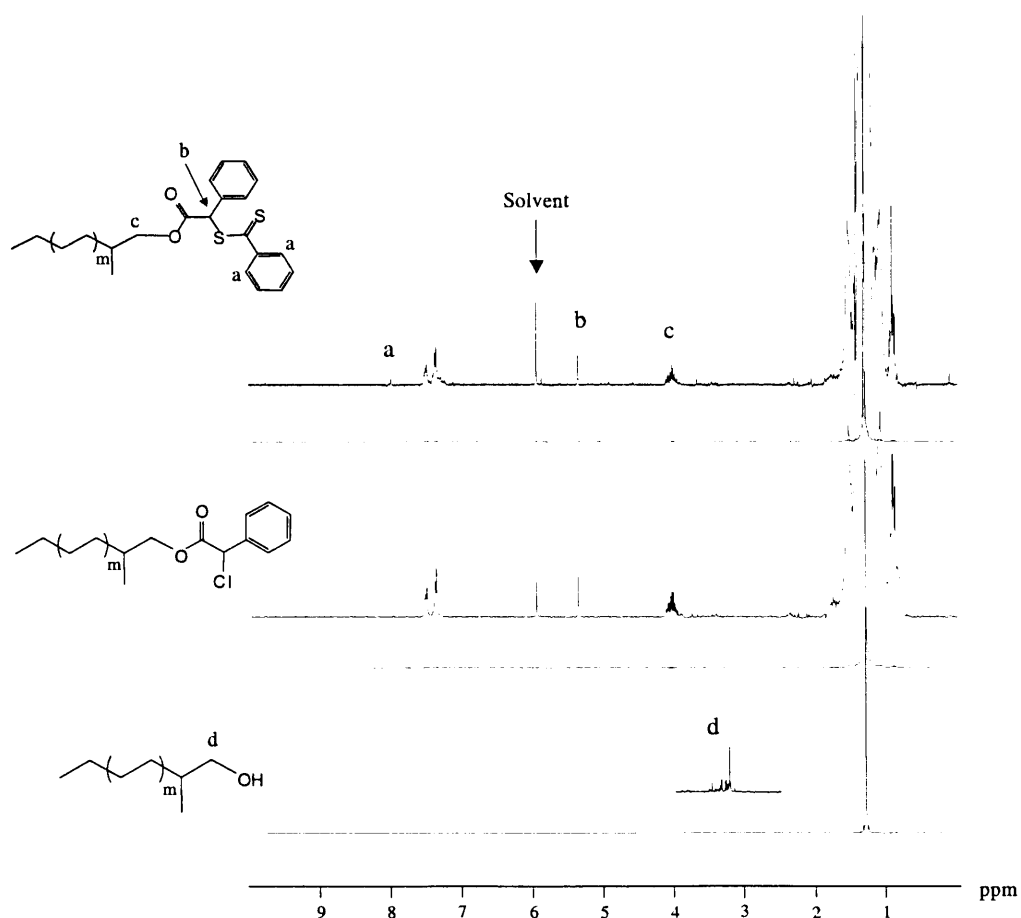


Figure 5-2 ^1H NMR spectra of PE-OH, PE-CPA and PE-CPDB

In FT-IR analyses of PE-CPA and PE-CPDB, the signals at 1760 and 1155 cm^{-1} were observed, assigned to carbonyl (C=O) and ether (C-O-C) groups, respectively, indicating the ester bond was in both polymers. From those results of analyses, it would be indicated that PE chain transfer agent (PE-CTA) possessing the dithiobenzoate group was synthesized by sequential functionalization of terminally hydroxylated PE.

RAFT polymerization of MMA initiated by AIBN

The author applied the RAFT polymerization method to create a polymer hybrid based on PO. The polymerization of MMA with PE-CTA was performed by using AIBN as an initiator at 60 °C in toluene under a slurry condition. The weight ratios of the PE-CTA to the AIBN were set at 1000/1 or 2000/1, and the weight ratio of total monomer to the PE-CTA was set at 10/3. The polymerization was stopped by cooling of reactor with ice bath. The polymerization mixture was poured into methanol, collecting all polymers. To remove homo-PMMA, the obtained polymers were purified with Soxhlet extractor with boiling THF. In both samples, there were observed some amounts of homo-PMMA (ca. 1-2g of homo-PMMA were collected by Soxhlet extraction with boiling THF). Table 5-1 summarizes the results of polymerization for two polymerization conditions. In both cases, the amounts of purified polymers after the Soxhlet extraction increased compared with the one of the PE-CTA as starting material.

Gel permeation chromatography (GPC) measurements revealed that the molecular weight (M_w) of the purified polymers increased from 36,600 by PE-CTA, to 38,500 and 40,000, respectively (shown in figure 5-3). The M_w/M_n ratios of the purified polymers were between 2.3 and 2.4, gotten smaller than one of the PP-OH, 2.84. These results would show the formation of PE-PMMA polymer hybrid via RAFT polymerization.

Table 5-1 Summary of MMA polymerization^{a)}

Run #	PE-CTA (g)	MMA (g)	AIBN (mg)	Yield ^{b)} (g)	PMMA Contents ^{c)} (wt% in polymer)	GPC ^{d)}		
						M_w	M_n	M_w/M_n
P-1	3.14	5.0	3.0	3.41	7.8	38,500	16,100	2.39
P-2	3.31	10.0	1.5	4.21	23.0	40,000	17,100	2.34
PE-OH	-	-	-	-	-	36,600	12,900	2.84

a) All polymerization were carried out at 60 °C for 24 hour in toluene. The total volume of each polymerization was 30 mL. b) after purification of obtained polymer samples by Soxhlet extractor with boiling THF. c) estimated by ¹H NMR measurement. d) GPC data (PE standard).

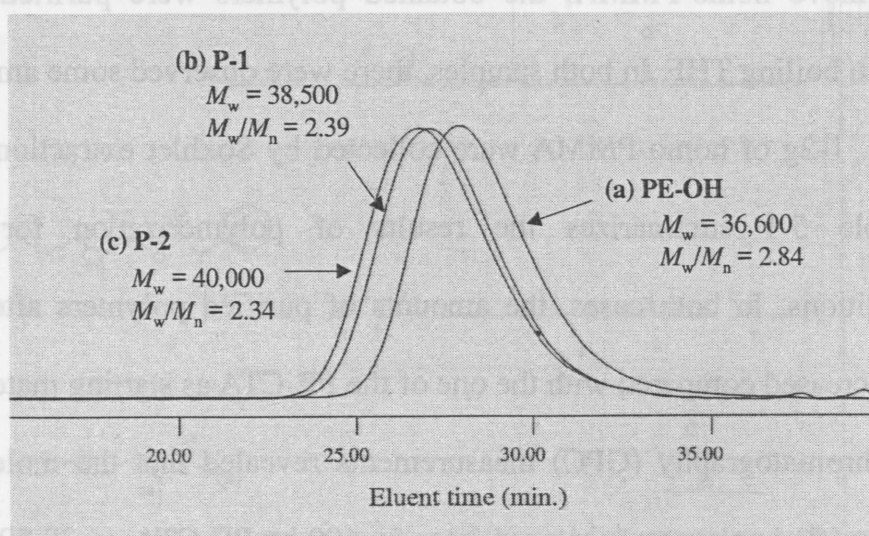


Figure 5-3 GPC traces of (a) PE-OH and purified polymers with PMMA contents of (b) 7.8 wt% (P-1) and (c) 23 wt% (P-2)

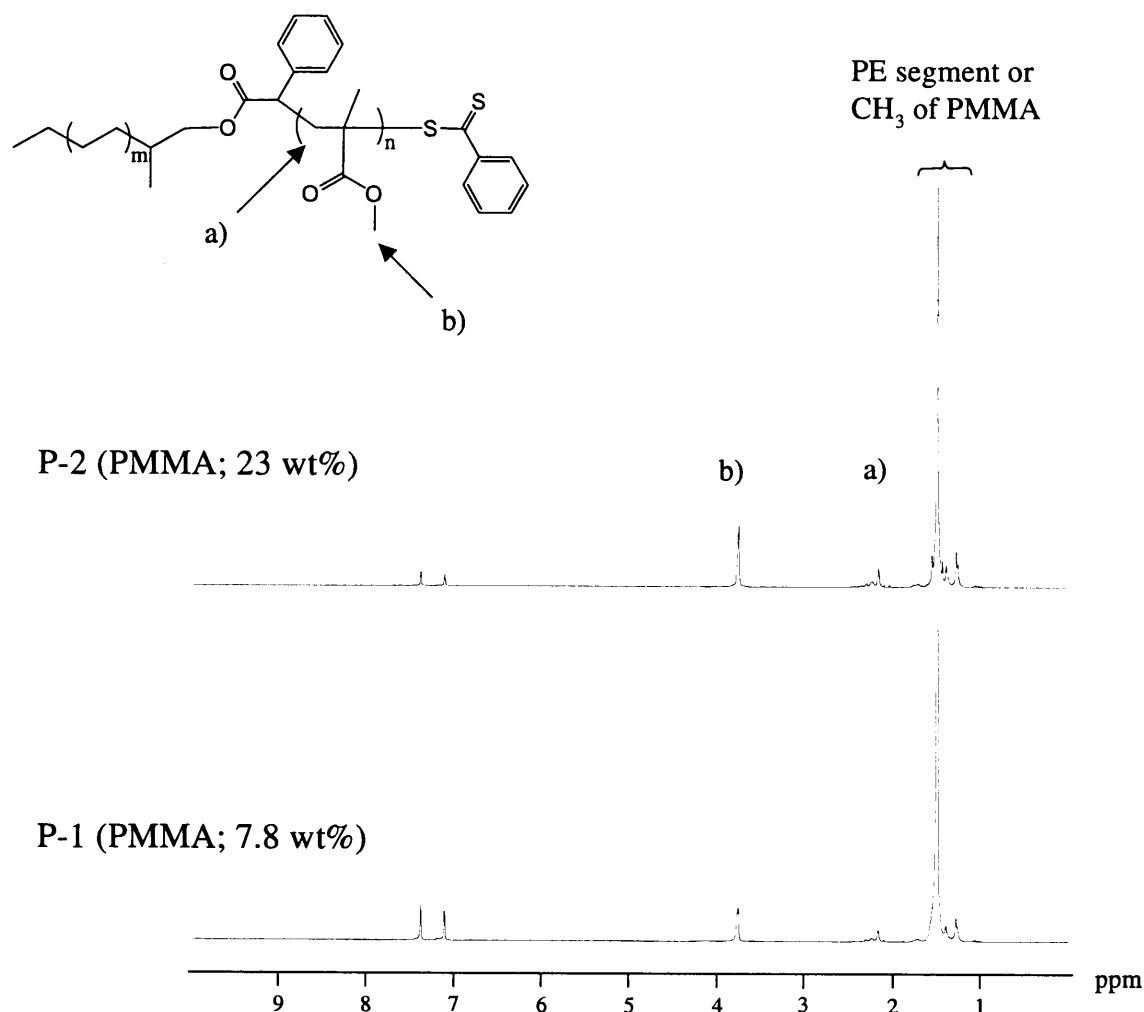


Figure 5-4 ¹H NMR spectra of purified polymer (PE-PMMA polymer hybrid)

The purified polymers were analyzed at 120 °C with ¹H NMR with ODCB as a solvent. The PMMA contents in the purified polymers were calculated at the ratio of two integrated intensities between 3.6 ppm (assigned to the methyl protons of the PMMA segment) and 1.3 ppm (assigned to the methylene protons of PE). From the ¹H NMR spectra shown in figure 5-4, the purified polymers contained 7.8 and 23 wt% of PMMA segment, respectively.

Microstructure of resulting polymers

Figure 5-5 shows TEM images of PE-CTA and purified polymers of PE-PMMA. In case of PE-CTA (before MMA polymerization), the lamella originated by PE was observed clearly. In purified polymers (after MMA polymerization), however, the nano-structures of them would change compared with PE-CTA, as like that the lamellar was come loose according to PMMA contents. In this study, MMA polymerization with PE-CTA was performed under a slurry condition. Therefore, it would be suggested from TEM images that PMMA chain was grown on the surface of PE-CTA particle and in parts of amorphous of PE-CTA.

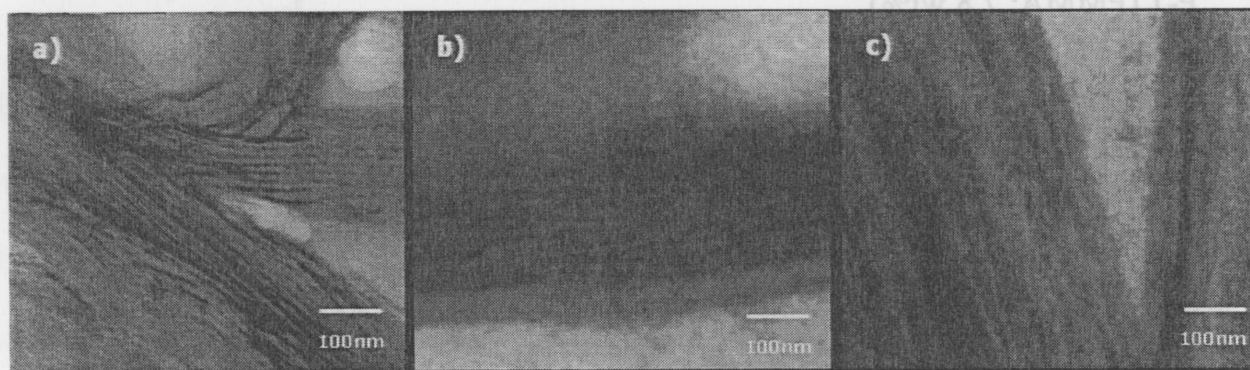
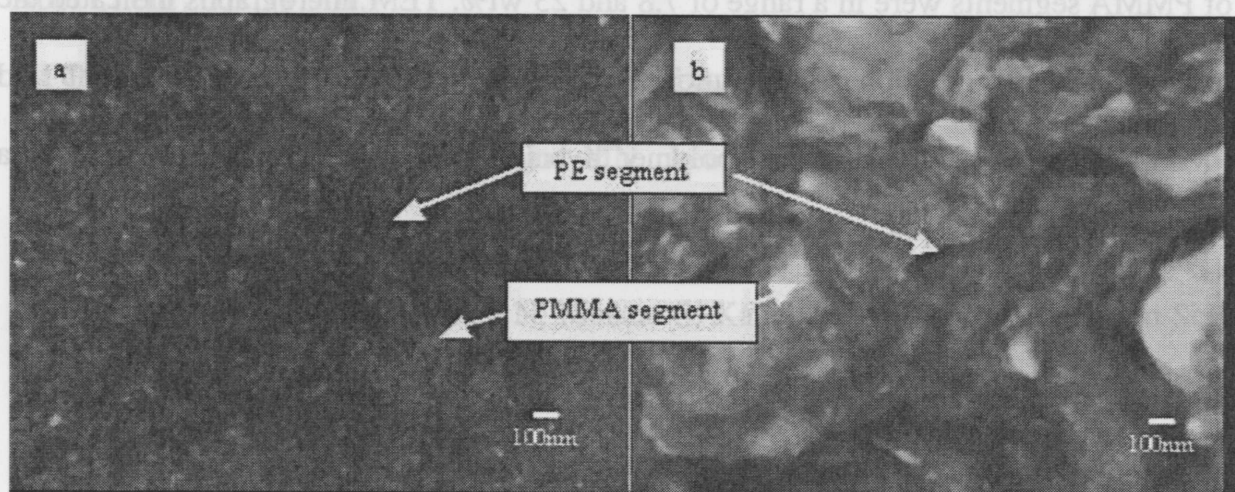


Figure 5-5 TEM images; a) PE-CTA and purified polymers with PMMA contents of (b) 7.8 wt% (P-1) and (c) 23 wt% (P-2)

Figure 5-6 shows TEM images of sheets of purified polymer with 23 wt% of PMMA contents and homo-PE/homo-PMMA blend polymer. Those sheets were prepared by the

press after anneal at 200 °C.

The TEM images of the purified polymer reveal the nanometer level microphase-separation morphology between the PE segment and PMMA segment different than PE/PMMA blend polymer, similar to PE-*b*-PMMA by ATRP in the author's previous paper [8]. That would be indicated that polymer hybrid based on PE was synthesized via RAFT polymerization, which is a metal free CRP method.



[10] Matsugi T, Kaneko H, Kojoh S, Ono SS, Inuta J, Nobori T, Kawahara N, Matsuo S. Figure 5-6 TEM images of polymer sheets; a) purified polymer (PMMA; 23 wt%), b) homo-PE / homo-PMMA blended polymer (PE/PMMA = 75/25 w/w) 2004;37:3651.

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4. Conclusion

PE-PMMA polymer hybrid was synthesized via RAFT polymerization method for the first time using PE-CTA that was prepared by sequential functionalization of terminally hydroxylated PE. The structure of PE-CTA was confirmed by ^1H NMR and FT-IR analyses. The results of GPC after MMA polymerization revealed that the molecular weight (M_w) of the purified polymers increased from 36,600 by PE-CTA, to 38,500 and 40,000, respectively. ^1H NMR analysis of purified polymers confirmed that the amounts of PMMA segments were in a range of 7.8 and 23 wt%. TEM micrographs indicated the nanometer level microphase-separation morphology between the PE segment and PMMA segment, suggesting that polymer hybrid based on PE was synthesized via RAFT polymerization method.

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Chapter 6

**Synthetic method of polypropylene-*graft*-polystyrene
(PP-*g*-PS) by coupling reaction with brominated
polypropylene**

1. Introduction

Recent advances in polyolefin (PO) chemistry have led to the creation of polymer hybrid linking between PO and polar polymer segments, bringing the ordinary PO some improved and unique properties to broaden the applications of PO to highly profitable fields such as compatibilizers, adhesion bonds, and so on [1-5].

While an effective strategy for improving the compatibility of immiscible polymer systems is the use of block or graft copolymers as compatibilizing agents [6, 7], the synthetic challenges in preparing well-defined block or graft polymers of POs has proven formidable. So far, the synthetic route of well-defined polypropylene-*graft*-polystyrene (PP-*g*-PS) has been reported in several papers. Chung has developed an interesting approach to polypropylene (PP) / polystyrene (PS) block and graft polymers by introduction of oxygen to a borane-functionalized PO [8-11]. A styrene-terminated PP has been adopted for atom transfer radical polymerization (ATRP) to prepare PP-*g*-PS after bromination [12]. Additionally, graft copolymer of PO-*g*-PS has been synthesized by the copolymerization of olefins with PS macromonomers by several scientists [13-16].

As part of the author's interest in developing a new and convenient methodology for the synthesis of well-defined PP-*g*-PS, the author was fascinated with the coupling reaction between functional polymers. In here, the synthesis method of PP-*g*-PS by coupling reaction was reported. At first, the author synthesized propylene/bromoundecene copolymer (PP-Br) using $\text{En}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system. Then, PP-*g*-PS was synthesized by the coupling reaction between PP-Br and polystyryl lithium salts (PS-Li) as a result of living anionic polymerization.

2. Experimental section

Materials

n-Butyllithium (n-BuLi) was purchased from Wako Pure Chemical Industries, Ltd. as hexane solution (1.54 M). 11-bromoundec-1-ene (Un-Br) was purchased from Aldrich Co. and purified by distillation under reduced pressure. Styrene was purchased from Wako Pure Chemical Industries, Ltd. and purified by the distillation with calcium hydride under reduced pressure. Other materials were same as mentioned above.

Analysis

Molecular weights of polymers were recorded on alliance GPC2000 and determined by gel-permeation chromatography (GPC) using o-dichlorobenzene as solvent. The detector was a differential refractive index detector. ^1H NMR spectra were recorded on a JEOL JNM GX-270 series in pulse Fourier transform mode using TCE as solvent. The ultimate viscosity of polymers was measured in decalin at 135 °C.

The peaks of melting temperatures of the polymers were measured with a Shimadzu DSC-60 differential scanning calorimeter. The samples were heated to 200 °C at 50 °C min^{-1} , maintained at 200 °C for 10 minutes, and cooled to 30 °C at 10 °C min^{-1} for recrystallization followed by reheating to 200 °C at 10 °C min^{-1} . To estimate the thermal history, the thermogram of each sample was recorded during the second heating run. The instrument was calibrated with the melting points of indium and lead.

TEM analysis was carried out with ultrathin (ca. 100 nm) sections of the polymer, which had been pressed into a sheet, were cut on a Reica Ultracut microtome equipped with a diamond knife at a low temperature and then were stained with RuO_4 . TEM observations were made with a Hitachi H-7000 transmission electron microscope at an

acceleration voltage of 75 kV.

Copolymerization of propylene with Un-Br (Typical procedure)

In a 500 ml reactor equipped with stirrer, gas inlet tube and thermometer, was placed 250 ml of toluene. The toluene was saturated with propylene at 40 °C, then 1.2 ml of 11-bromoundec-1-ene (5 mmol), 13.5 ml of MAO in toluene solution (20 mmol as [Al]) and $\text{En(Ind)}_2\text{ZrCl}_2$ (0.02 mmol) were added to the reactor. The polymerization was performed at that temperature under constant propylene monomer gas feed (100 NL/h). After 30 min., the polymerization was stopped by addition of 20 ml of isobutanol to the reactor. The reaction mixture was poured in 1 l. of acidic methanol. The resulting polymer was collected by filtration and washed with methanol, then dried at reduced pressure (160mmHg) at 80 °C for 10 hours.

Coupling reaction (Typical procedure)

In a 200 ml Schlenk Flask equipped with magnetic stirrer was placed 3.37 g of styrene (32.3 mmol) and 100 ml of toluene. 2.17 ml of n-BuLi in hexane solution (1.54 M; 3.34 mmol) was added to the solution. The polymerization was performed at 0 °C for 15 min. and at r.t. for 15 hours with stirring. In a 500 ml glass reactor equipped with mechanical stirrer was placed 1.00 g of the PP-Br (Pol-1, [Br]: 0.34 mmol). The PP-Br was diluted in 200 ml of toluene at 80 °C. The styrene polymerization solution that was obtained with the above procedure was added to the PP-Br toluene suspension. The reaction mixture was stirred at 80 °C for 6 hours. After that, it was poured into 1 l. of methanol. The obtained polymers were purified with boiling THF by Soxhlet extractor for 16 hours, and dried at 80 °C in a vacuum for 10 hours. 1.31 g of purified polymer

was obtained.

Polymer blend

The blended polymers, used for TEM images, were prepared with 0.42 g of PP-Br (Pol-1) and 0.42 g of PS ($M_w = 5,500$; $M_w / M_n = 1.05$) with or without 0.084 g of PP-g-PS in solution to obtain molecular-level mixing. The polymers and o-xylene (50 ml) were added to a 100 ml, round-bottom flask equipped with a stirring bar and were stirred at 130 °C until the polymer mixture was homogeneous for 2 hours. The blended polymer was precipitated into methanol, and then dried at 80 °C for 10 hours in a vacuum.

3. Results and discussion

Synthesis of the PP-g-PS copolymer

The synthesis of PP-g-PS involved two steps (figure 6-1), namely, olefin polymerization and a coupling reaction.

The first step in the preparation of the graft copolymer concerns the synthesis of suitable propylene copolymers containing Un-Br with a metallocene catalyst. A series of copolymerizations were performed under variable monomer feed ratios, in the presence of $\text{En(Ind)}_2\text{ZrCl}_2$ activated by MAO, to obtain the copolymers with variable composition. The amounts of comonomer contents in resulting polymers were estimated by ^1H NMR analysis as shown in figure 6-2 (a). The multiple peaks of 3.2 - 3.4 ppm were assigned to methylene ($-\text{CH}_2\text{-Br}$) adjacent to the bromine atom. The result of copolymerization was summarized in table 6-1. Resulting polymers contained comonomer, Un-Br, at a range from 1.5 to 10.3 mol %, that were proportional to the

amounts of comonomer used in polymerization. And, the values of molecular weight distribution (M_w / M_n) of copolymers were under 2.

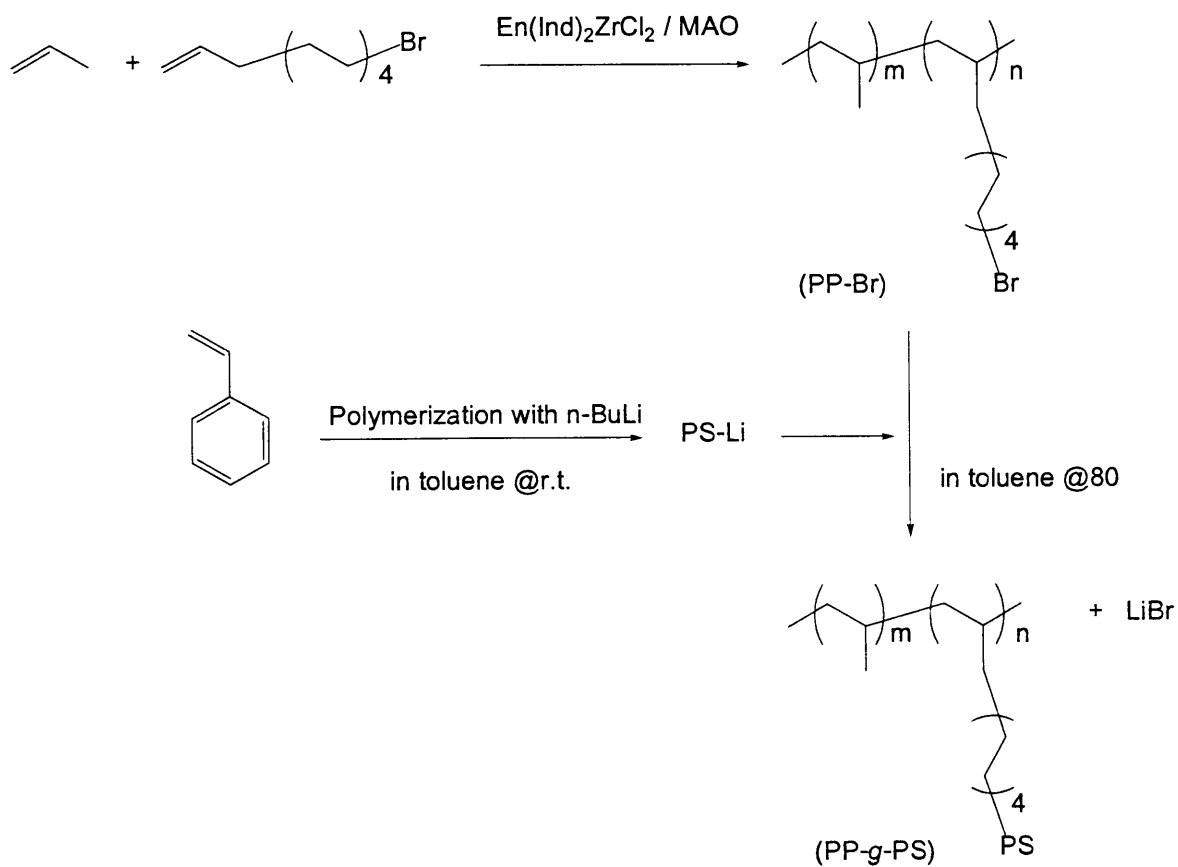


Figure 6-1. The synthetic pathway for preparing PP-g-PS copolymers

The graft copolymers (PP-*g*-PS) were obtained through the coupling reaction of PP-Br and polystyryl lithium salts (PS-Li). Styrene polymerization was performed with *n*-butyllithium as initiator at r.t. in toluene as a living nature. Without quenching of polymerization solution, it was mixed into the suspension of PP-Br in toluene. After the coupling reaction, the reaction mixture was poured into methanol, collecting all polymers. To remove homo-PS, the obtained polymers were purified by Soxhlet extractor with boiling THF. Table 6-2 summarizes the results of the coupling reactions.

Table 6-1 Results of propylene and Un-Br copolymerization^{a)}.

Run No.	Un-Br (mmol)	Activity (kg/mol[Zr]/h)	M_w ^{b)} (g/mol)	M_w/M_n	Comonomer ^{c)} Contents (mol %)	T _m (°C)
Pol-1	5	1851	19600	1.87	1.5	131.7
Pol-2	11	853	14900	1.77	3.9	111.7
Pol-3	21	624	11200	1.84	10.3	87.4
Pol-4	-	4636	30100	1.72	-	133.9

a) Polymerization condition; Metallocene (En(Ind)₂ZrCl₂, 0.02 mmol), MAO (20 mmol), Hexane (250 mL), 40 °C, 30min. b) Determined by GPC (PS standard).

c) Determined by ¹H NMR.

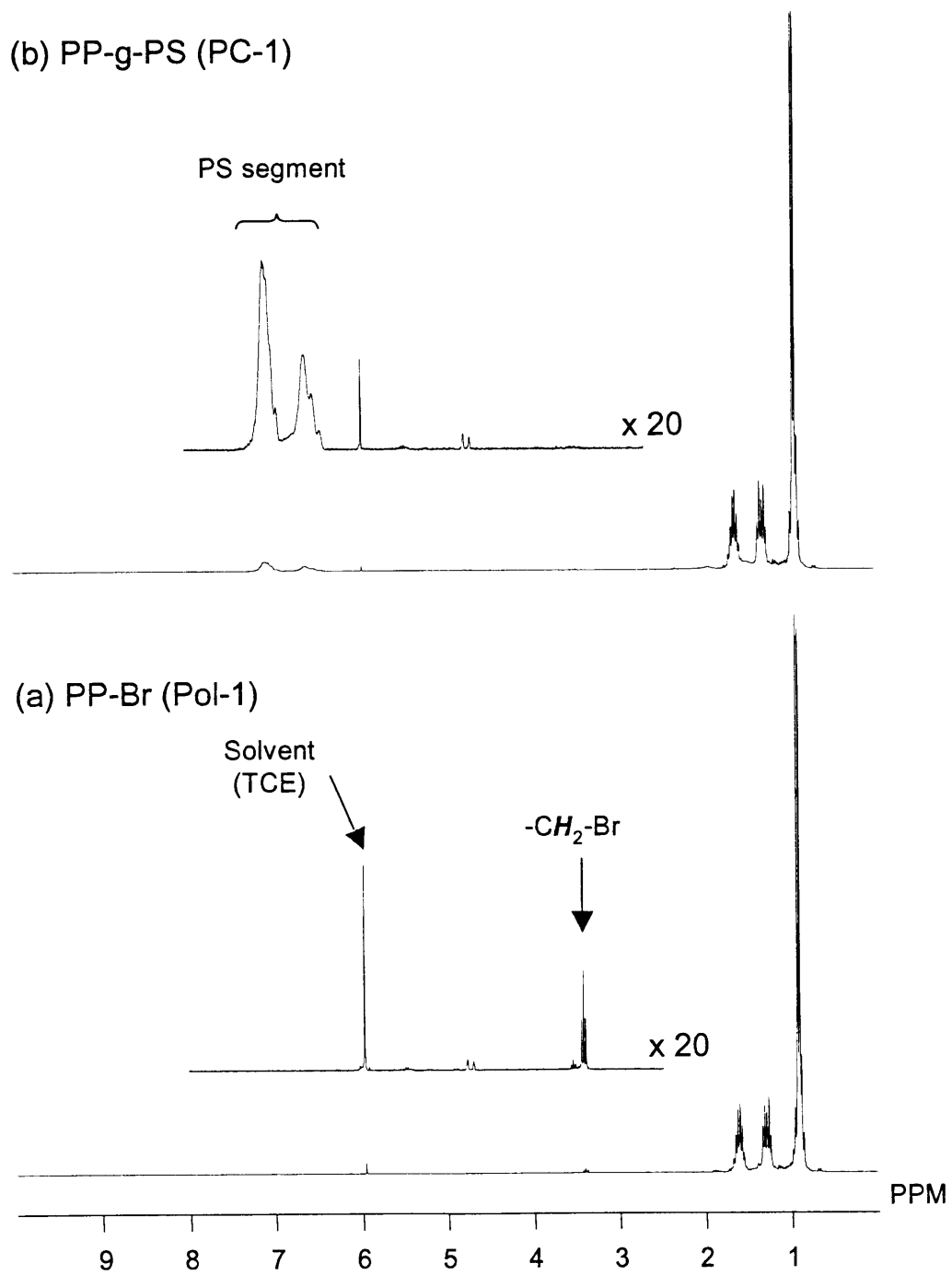


Figure 6-2 ¹H NMR spectra of PP-Br and PP-g-PS

In both cases, the amounts of purified polymers after the Soxhlet extraction increased compared with the PP-Br starting material. The ^1H NMR analysis of the resulting polymers (figure 6-2(b)) indicated that the PS segment was included in the resulting polymer, because new peaks appeared from 6.6 ppm to 7.7 ppm, and that the bromine atom was consumed because the peaks of 3.2 - 3.4 ppm disappeared, suggesting that PS-Li reacted with the bromine atom. From the ^1H NMR analysis, the purified polymers contained 20 and 51 wt% of PS segment, respectively. It was also suggested by the measurement of ultimate viscosity that molecular weights of the resulting polymers were increased beyond what the weights were as starting materials [17]. Those results show that PP-*g*-PS was synthesized by a coupling reaction.

Table 6-2 Results of coupling reaction^{a)} of PP-Br and PS-Li

Run No.	Styrene Polymerization ^{b)}				PP-Br (g)	Yield ^{d)} (g)	PS contents ^{e)} (wt%)	[η] (dl/g)	T _m (°C)
	Styrene (mmol)	n-BuLi (mmol)	M_w ^{c)}	M_w/M_n					
PC-1	33	3.4	1100	1.12	1.00	1.31	20	0.24	129.9
PC-2	161	3.4	4900	1.08	1.00	2.39	51	0.28	127.1
Pol-1							-	0.22	131.7

a) Reaction condition; 80 °C, in toluene, 6 hr. b) Polymerization condition; ambient temperature, in toluene, 15 hr. c) Determined by GPC (PS standard). d) After purification by Soxhlet extraction. e) Determined by ^1H NMR.

Morphology of PP-g-PS copolymer

Figure 6-3 shows TEM micrographs of two PP-g-PS copolymers (PC-1 and PC-2). TEM images of the PP-g-PS copolymers reveal the microphase-separation morphology at the nanometer level between the PP segment and the PS segment. That would also indicate that PP-g-PS was synthesized.

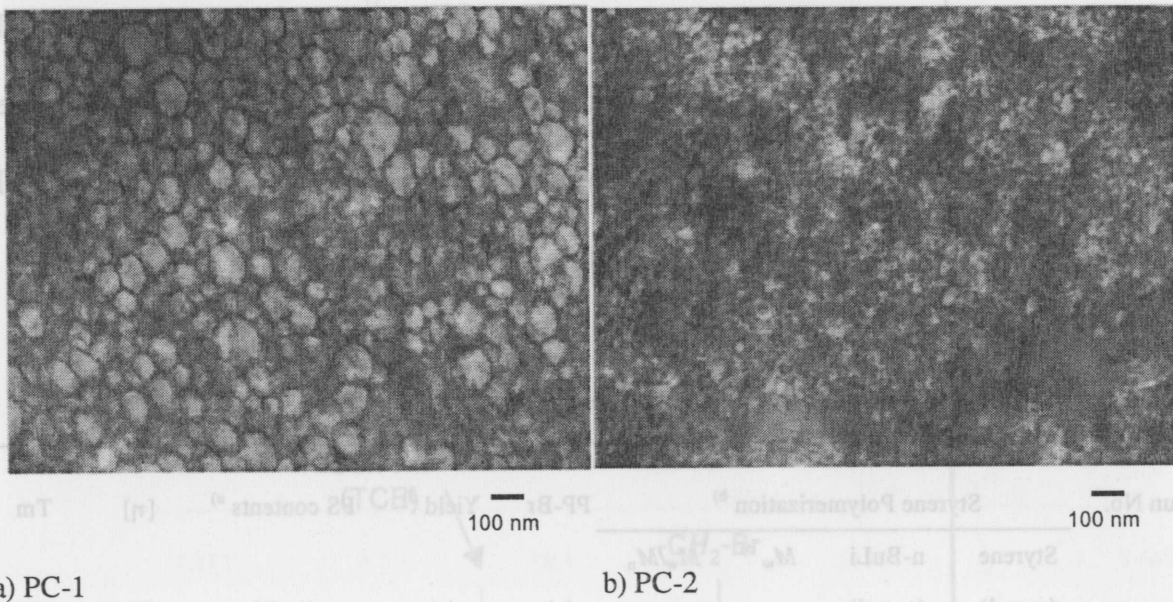
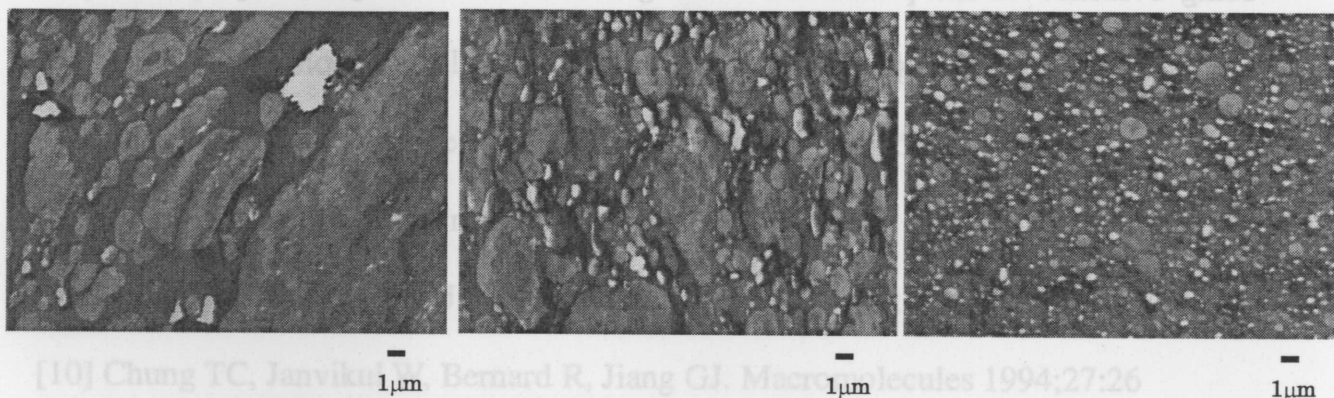


Figure 6-3 TEM images of a PP-g-PS polymer sheet

Obtained block copolymers were expected to work as a compatibilizer for improving the interfacial interactions between blended polymers. To estimate this effectiveness, the author blended the PP-g-PS copolymer and homo-PP and homo-PS (homo-PP/homo-PS/PP-g-PS = 5/5/1 wt ratio) at 130 °C in o-xylene. For comparison, a blended sample without PP-g-PS (homo-PP/homo-PS = 5/5 wt ratio) was also prepared. Figure 6-4 shows TEM images of these blended polymers. The blended polymers

containing PP-g-PS showed morphology in which the size of the dispersed domains was smaller than that of the blended polymer without PP-g-PS. And the PS domain in PC-2 was finely dispersed compared with PC-1. It can also be suggested that the size of the domain in the PP/PS blended polymer depended on the PS contents of PP-g-PS. These results indicate that such PP-g-PS copolymers effectively improve the compatibility between PP and PS.



a) PP/PS blend (5/5 wt ratio) b) PP/PS/PC-1 (5/5/1 wt ratio) c) PP/PS/PC-2 (5/5/1 wt ratio)

Figure 6-4 TEM images of PP/PS polymer sheet with or without PP-g-PS

4. Conclusion

The new synthetic method of PP-*g*-PS copolymers has herein been described. The PP-*g*-PS was synthesized by the coupling reaction of the PP-Br produced by metallocene-catalyzed copolymerization and PS-Li made by living anionic polymerization. These structures were confirmed by ¹H NMR analysis. TEM micrographs of PP-*g*-PS copolymers indicated the nanometer level microphase-separation morphology between the PP segment and the PS segment, thus being evidence of the production of PP-*g*-PS. Obtained PP-*g*-PS copolymers could function as effective compatibilizers of PP and PS.

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[17] In this study, the author adopted the ultimate viscosity to evaluate molecular weights of PP-*g*-PS copolymer because it's difficult to measure molecular weights of the copolymer by GPC due to the detector.

General Conclusion

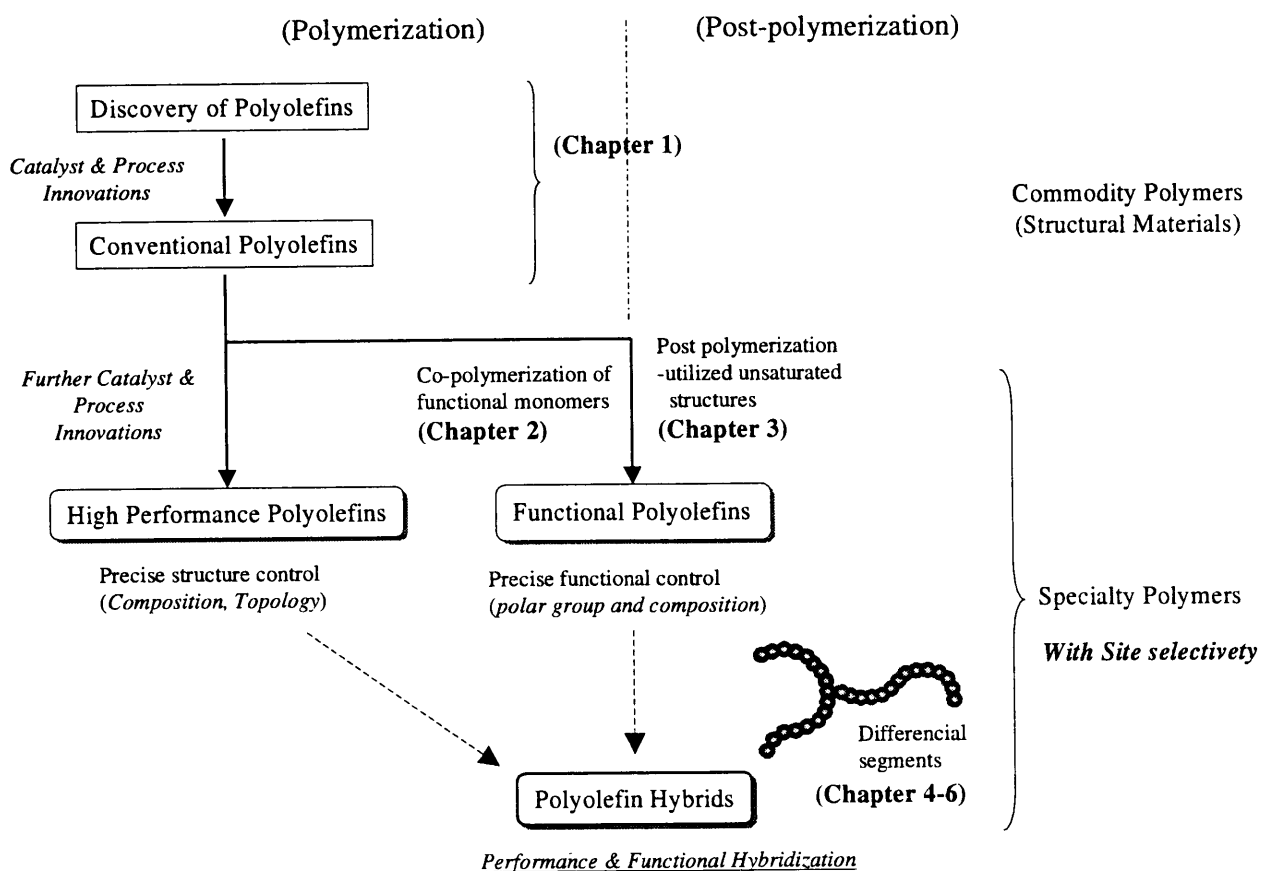
This thesis has dealt with the study on microstructures of polyolefins and synthesis of functionalized polymers based on polyolefins. This concerns the investigation of insertion reaction of polar monomer into the metallocene catalyst. The distinction of complicated unsaturated structures and the investigation of chain end structures of polyolefins are also discussed. Those studies are aimed to create well-defined functional polymers. Furthermore, the creation of functionalized polyethylene and polypropylene are discussed, too.

To explain this thesis in plain scheme (scheme 1), the author classified polyolefin materials into two categories, commodity polymers and specialty polymers. The author also grouped the methodology for the improvement of properties of polyolefins into two types, namely polymerization and post-polymerization. The framework of this thesis and the brief conclusions of each chapter are as follows.

Chapter 1 reviews the historical aspects of polyolefins from the discovery of polyolefins to latest high performance materials.

In chapter 2, as preliminary study related to copolymerization of functional monomers, the insertion reaction of 10-Undecen-1-ol protected with TMAL, TEAL, TNBAL or TIBAL (Un-O-AlR_2 ; R = Me, Et, n-Bu, i-Bu) into the metallocene active center of $\text{En(Ind)}_2\text{ZrCl}_2/\text{MAO}$ has been confirmed by GC and NMR analyses. In the case of TEAL, TNBAL and TIBAL, the identified compounds in which alkyl groups derived from trialkylaluminum were incorporated into Un-OH. It could be concluded that Un-O-AlR_2 was inserted into the metallocene active center catalytically with an alkyl exchange reaction in the absence of olefin monomers.

Methodology flow of polyolefins to specialty polymers
and related chapters in this thesis



Scheme 1

In chapter 3, in polypropylene and other polyolefins, unsaturated structures that were utilized in post-polymerization reaction to synthesize functional polymers have been investigated. The vinylidene structures in metallocene-catalyzed polypropylenes have been analyzed by ^1H NMR. The internal and terminal vinylidene structures were clearly distinguished using ODCB as solvent due to the effect of the ring current, and the vinylidene structure next to the chain end could be assigned for the first time as different peaks from the other vinylidene structures. $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ tended to

produce internal vinylidene structures compared with $\text{En}(\text{Ind})_2\text{ZrCl}_2$. Propylene homopolymerizations have also been conducted with three kinds of metallocenes to discuss the chain end structures of the polymer and the mechanism of polymerization. In the polymerization with Cp_2ZrCl_2 , the termination reaction exclusively occurred at 1,2-inserted chain end. In cases of $\text{En}(\text{Ind})_2\text{ZrCl}_2$ and $\text{iPr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$, besides at 1,2-inserted site, a considerable number of termination reactions occurred at 2,1-inserted chain end. Internal vinylidenes were detected in both metallocenes. Moreover, i-butenyl group and internal tri-substituted alkenyl group were identified in $\text{En}(\text{Ind})_2\text{ZrCl}_2$ and $\text{iPr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$, respectively. Those structures would be formed via π -allyl complex between the metal center of the catalyst and the growing polymer chain with liberation of hydrogen. Furthermore, hexene, 4-MP-1 and 3-MP-1, homopolymerizations have been conducted with metallocenes: $\text{En}(\text{Ind})_2\text{ZrCl}_2$ and $\text{iPr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$. ^1H NMR analyses of the resulting polymers were carried out to identify the unsaturated structures of those polymers. In polyhexene and poly(4-MP-1), the di-substituted vinylene structure (2Vn) was mainly observed. On the other hand, in poly(3-MP-1), the tri-substituted vinylene (3Vn), vinylidene (Vd) and vinyl (Vn) structures were identified for the first time.

In chapter 4, to create novel olefinic polymer hybrids, it has been described that a new synthetic route for polyolefinic graft block copolymers by adopting coupling reaction between terminally hydroxylated polyolefins and maleic anhydride grafted polyolefins. Terminally hydroxylated polypropylene (PP-OH) was coupled with PE-g-MAH and such EPR-g-MAH to give polyolefinic graft block copolymers (PE-g-PP and EPR-g-PP, respectively). The formation of PE-g-PP was confirmed by enhancement on molecular weight compared with the corresponding polymer blend. It

brought about distinctively decrease in size of dispersed domain in its phase separation morphology. Occurrence of coupling reaction to give EPR-g-PP was indicated by extreme decrease in its solubility to decane in comparison with the corresponding polymer blend. It led to unique morphology demonstrating lamella microstructure that had never been reported for a comparable polyolefin composite.

In chapter 5, PE-PMMA polymer hybrid, polyolefin and non-polyolefin grafted block copolymer, has been synthesized via RAFT polymerization method for the first time using PE-CTA that was prepared by sequential functionalization of terminally hydroxylated PE. The structure of PE-CTA was confirmed by ^1H NMR and FT-IR analyses. The results of GPC after MMA polymerization revealed that the molecular weight (M_w) of the purified polymers increased from 36,600 by PE-CTA, to 38,500 and 40,000, respectively. ^1H NMR analysis of purified polymers confirmed that the amounts of PMMA segments were in a range of 7.8 and 23 wt%. TEM micrographs indicated the nanometer level microphase-separation morphology between the PE segment and PMMA segment, suggesting that polymer hybrid based on PE was synthesized via RAFT polymerization method.

In chapter 6, the new synthetic method of PP-g-PS polymer hybrid, polyolefin and non-polyolefin grafted block copolymer, has been described. The PP-g-PS was synthesized by the coupling reaction of the PP-Br produced by metallocene-catalyzed copolymerization and PS-Li made by living anionic polymerization. These structures were confirmed by ^1H NMR analysis. TEM micrographs of PP-g-PS copolymers indicated the nanometer level microphase-separation morphology between the PP segment and the PS segment, thus being evidence of the production of PP-g-PS. Obtained PP-g-PS copolymers could function as effective compatibilizers of PP and PS.

So far, the properties of polyolefins have been improved by catalyst systems and process innovations concerning the polymerization reaction. However, it would be still hard to overcome their weak points as a lack of compatibility with other polar materials by polymerization methodologies. On looking ahead to the near future, one of the most possible approaches to create special polymers is post-polymerization reactions with a site selectivity. As the results in this thesis, microstructures of polyolefins, especially unsaturated structures, are to be clearly. Those knowledges would contribute for site selective functionalization, which is one of post-polymerization reactions, of polyolefin materials. Furthermore, synthetic methods of polymer hybrids possessing polyolefin segment and other nature segment such as RAFT polymerization and coupling reaction are proposed. Those hybrid materials based on polyolefins would be broaden their possibility for applications in industry.

The author convinces that obtained results in this thesis would be helpful for creation of functional polyolefins overcome their disadvantages. Those materials seem to possess several benefits, namely energy-saving in fabrication of polymer, process simplification and the totally save of the oil resource by broaden application of olefinic materials that are easy to recycle. The author also hopes that produced new polymers are effective for our future lives.

List of Publication

Papers

1) N. Kawahara, S. Kojoh, S. Matsuo, H. Kaneko, T. Matsugi, N. Kashiwa:

“Investigation of insertion reaction of 10-undecen-1-ol protected with alkylaluminum in $\text{En}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system”

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2) N. Kawahara, S. Kojoh, Y. Toda, A. Mizuno, N. Kashiwa:

“The detailed analysis of the vinylidene structure of metallocene-catalyzed polypropylene”

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3) N. Kawahara, S. Kojoh, S. Matsuo, H. Kaneko, T. Matsugi, Y. Toda, A. Mizuno, N. Kashiwa:

“Study on chain end structures of polypropylenes prepared with different symmetrical metallocene catalysts”

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4) N. Kawahara, J. Saito, S. Matsuo, H. Kaneko, T. Matsugi, Y. Toda, N. Kashiwa:

“Study on unsaturated structures of polyhexene, poly(4-methylpentene) and poly(3-methylpentene) prepared with metallocene catalysts”

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5) N. Kawahara, S. Kojoh, S. Matsuo, H. Kaneko, T. Matsugi, J. Saito, N. Kashiwa:

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6) N. Kawahara, J. Saito, S. Matsuo, H. Kaneko, T. Matsugi, S. Kojoh, N. Kashiwa:

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