

Effects of External Electron Donor on Catalyst Active Sites in Propylene Polymerization

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ABSTRACT: In order to investigate the effects of an external electron donor on catalyst active sites in propylene polymerization, physical properties of the produced polymers are measured with various techniques. From the thermal analysis and gel permeation chromatography (GPC) measurement, it is found that an external electron donor transfers the catalyst active sites from atactic sites via low isospecific sites to high isospecific sites. There are some differences between gas and slurry phase reactions. This may be due to the differences in diffusion phenomena with polymerization types. Polymer crystalline formations, such as spherulite and lamella structure, are observed by an image analyzer and closely coincide with the GPC results in molecular weight of polypropylene. From the results of ultraviolet visible (UV VIS) and Fourier transform infrared (FTIR) experiments, it is found that some complexes are formed between cocatalyst and the external electron donor, and it is supposed that those complexes are strongly associated with catalyst active site transition. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1779–1787, 1998

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INTRODUCTION

Various types of Ziegler–Natta catalysts are prepared by their unique preparation process. These result in various types of active sites, which have different electric and stereospecific properties. Therefore, the structures and distributions of polymer are directly related to the properties of catalyst active sites; that is, polymers that have various molecular weights and side chains are produced.¹ These are intrinsic properties resulting from Ziegler–Natta catalyst. Accordingly, changing a process parameter is the only method for controlling polymer properties (i.e., reaction types, reaction temperature, reaction pressure,

concentrations of cocatalyst, and external electron donor, hydrogen partial pressure, etc.). Therefore, wide ranges of these factors must be considered to get the optimum polymerization conditions and polymers.

In general, external electron donors are known as selective atactic site poisoners and/or have the function of active site transition. Therefore, the polymer isotactic index is increased relatively, and the polymer yield is decreased. However, there is not any definite elucidation about the role of external electron donors on catalysis. For instance, Keii² reported that an external electron donor poisons the atactic sites selectively, resulting in an increase of the relative isotactic index. Also, polymer molecular weight increases because the cocatalyst amount is decreased by formation of complexes with the electron donor. Kashiwa,³ however, reported that there is no

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atactic site poisoning; instead, atactic site conversion to isotactic site occurs so that polymerization rate is increased on the isotactic site. Pino et al.⁴ also report that a low isospecific site is converted into a high isospecific site regardless of atactic site. On the other hand, Soga and Park⁵ insist that an atactic site is converted to an isotactic site without affecting reaction rate; and Härkönen et al.⁶ report that the electron donor poisons the atactic sites with formation of new isotactic sites. Besides these results, various explanations of the role of electron donor are reported.^{7–14}

As discussed above, there is not any consistency in the external electron donor addition effects on catalyst, and most of the results are obtained from slurry phase polymerization. However, there may be some differences in the effects of external electron donor on catalyst with polymerization types. Therefore, in this study, gas and slurry phase polymerizations are carried out respectively in a continuously stirred bed reactor (CSBR). Various polymer characterization techniques focusing on polymer molecular weight are used for proving the role of the external electron donor on the third-generation Ziegler–Natta catalyst. At this time, the characterized polymer is isotactic polypropylene (IPP) because characterization of IPP gives some information about the catalyst active site.

EXPERIMENTAL

Catalyst and Reagents

The catalyst used is the third-generation Ziegler–Natta commercial catalyst, named “HCAT.” It is kept in mineral oil to avoid O₂ and H₂O contact (39.5 wt % catalyst in oil and 2.55 wt % Ti on catalyst). Tri-ethylaluminum (TEAL) and para-ethoxyethylbenzoate (PEEB) are used as cocatalyst and external electron donor without any purification and are diluted to 1 and 0.1M in *n*-hexane, respectively. Sodium slice and benzophenone (Janssen Chimica, Belgium) are used for purification of *n*-hexane. Propylene used as monomer is polymer grade, and methanol is used as a polymerization quenching material. All of the gases used throughout this study are ultrahigh purity; molecular sieve 5A, and Ridox (Fisher, U.S.A.) traps are used for removing traces of water and oxygen in gases.

Activity Measurement

Propylene (PP) polymerization is carried out in a high-pressure reactor (Autoclave, U.S.A.) of 1 liter made of stainless steel. For the purpose of obtaining a uniform dispersion of catalyst in the reactor, glass beads of 2 mm o.d. are added to about 50 cc, which almost submerges the impeller of the anchor type. In order to confirm the mixing condition in the reactor, a simulated experiment is carried out in a transparent glass reactor, and excellent fluidization is observed. Accordingly, any doubts of mixing effect can be eliminated. All of the polymerization results adopted in this study are the average values of five trials. Reaction rate is measured by a mass flow controller (MFC) connected to a PC with an A/D converter, and expressed as g C₃H₆ per g Ti per h. In order to maintain reaction pressure (100 psi), a gas booster is used. All materials used are treated in a glove box. In order to simulate the practical plant process (separate injection of each material), the catalyst, cocatalyst, and electron donor are injected separately into the reactor until reaching the set point reaction condition. At the end of polymerization, it is quenched by methanol (introduced by high-pressure liquid pump into the reactor) to prevent further reaction. Polypropylene yield is evaluated as g PP per g Ti per h after vacuum drying at 50°C for 12 h.

Reaction conditions in these experiments are as follows: the reaction temperature is 40°C, the reaction pressure is 100 psi, the TEAL-to-Ti mole ratio is 100, and the PEEB to TEAL mole ratio is 0–0.1 (divided by four steps). For slurry phase polymerization, 300 cc of purified *n*-hexane is introduced into the reactor by a high-pressure liquid pump, and the reaction conditions are the same for the gas phase polymerization.

Physical Properties of Polymer

Isotactic indices of polymer produced are measured by the xylene extraction method. In order to compensate for the results from the xylene extraction method, Fourier transform infrared (FTIR) (Perkin–Elmer system 2000) analysis is carried out [comparison of the absorbance band intensities between wave number = 998 (isotactic helix) and 973 (internal reference) cm⁻¹].¹⁵ A melting point of polymer is measured by differential scanning calorimetry (DSC) (Perkin–Elmer DSC7) in the temperature ranges of 30–220°C, and gel permeation chromatography (GPC) (Wa-

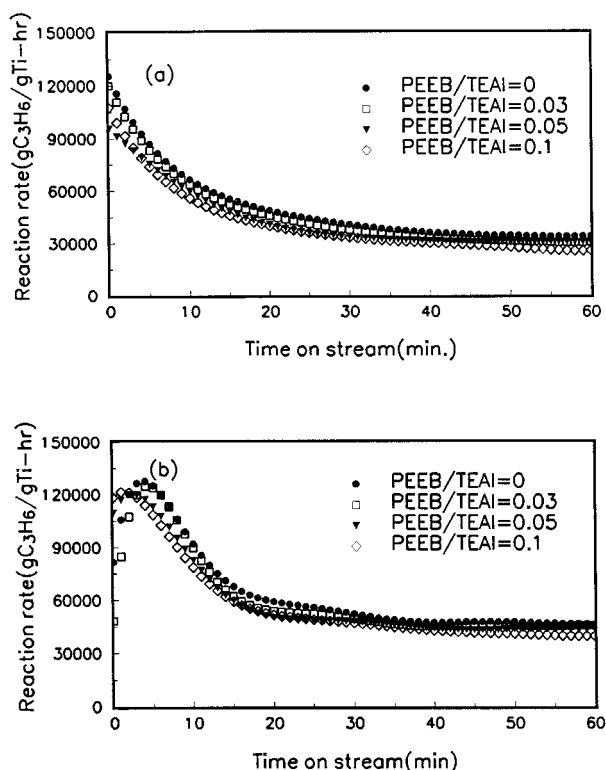


Figure 1 Kinetic curve patterns with the PEEB-to-TEAL mole ratio: (a) gas phase; (b) slurry phase. Pressure = 100 psig; temperature = 40°C; TEAL to Ti = 100; H₂ to C₃H₆ = 0.

ters 150°C) analysis is carried out for determining molecular weight and molecular weight distribution of polymer. Polymer crystalline form, such as spherulite and lamella structure, is observed by an image analyzer (Carl Zeiss, Jenaval). In order to investigate the possibility of complex formation between TEAL and PEEB, FTIR (Perkin-Elmer system 2000) and ultraviolet visible (UV VIS) analysis (Hitachi) are used.

RESULTS AND DISCUSSION

Reaction Rate, Polymer Yield, and Isotactic Index

Gas and slurry phase propylene polymerization were carried out to investigate reaction rate changes before and after the addition of external electron donor. As shown in Figure 1, reaction rate decreased with increasing the amount of electron donor. It is well known that the addition of electron donor generally decreases the reaction rate, and the reasons are well explained by Keii²: atactic sites on catalyst are selectively poisoned

by external electron donor so that total numbers of active sites are diminished. It is also found that sudden deactivation occurs as soon as maximum reaction rate is reached. This can be explained by chemical phenomena, such as active site reduction from Ti⁺⁴ to Ti⁺³ or Ti⁺² by cocatalyst.¹⁶⁻¹⁸ However, physical phenomena must not be ignored to explain this deactivation. That is, a polymer shell is formed around the catalyst particle with reaction time, and then monomers have difficulties in diffusion to the catalyst surface through the polymer shell.¹⁹ The same phenomena are found in slurry phase polymerization. Meanwhile, there are some differences in kinetic curves between gas and slurry phase polymerizations: the time of reaching maximum reaction rate in a slurry phase is longer than that in a gas phase. This can be explained as follows: there is nothing between catalysts, cocatalysts, and monomers in gas phase polymerization. Therefore, catalyst activation by cocatalyst progresses rapidly. However, in a slurry phase reaction, *n*-hexane is present between catalysts, cocatalysts, and monomers as liquid pool; so monomer and cocatalyst have difficulty in diffusion into the catalyst surface. In order to investigate the effect of an external electron donor on polymer physical properties, various characterization techniques are employed. First of all, isotactic index and polymer yield are measured, as shown in Figure 2. In the gas phase, polymer yield decreased by increasing the PEEB-to-TEAL mole ratio. On the other hand, isotactic index is increased. This result can be explained by Keii's theory, as follows²: atactic sites on catalyst are selectively poisoned by the electron donor so that isotactic index is increased relatively. In the slurry phase, polymer yield shows the same pattern with gas phase. However, the isotactic index pattern is different with the gas phase; severe changes of isotactic index are not found with the PEEB-to-TEAL mole ratio, and it shows a very high isotactic index, above 99%. This is due to dissolving of atactic polypropylene in *n*-hexane as soon as produced. Therefore, all PP obtained by slurry phase reaction is isotactic polymer. From these results, it is thought that there is little effect of an external electron donor in slurry phase polymerization. Practically, it is well known that a recovery process for atactic polymer is necessary in industrial plants.

Thermal Analysis by DSC

In general, thermal behavior of the polymer (melting point, crystallization temperature, crys-

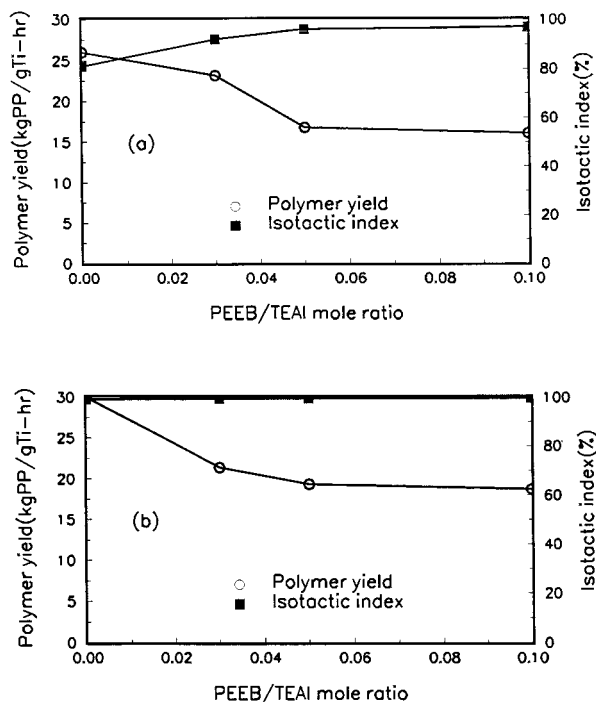


Figure 2 Relationship of polymer yield and isotactic index with the PEEB-to-TEAL mole ratio: (a) gas phase; (b) slurry phase.

tallinity, etc.) is closely related with its molecular weight.^{20,21} Especially, the polymer molecular weight can be predicted by measurement of polymer melting point. In this study, therefore, the melting point of IPP produced by xylene extraction is measured by DSC before investigation of its molecular weight. Figure 3 shows the results of DSC analysis of IPP produced by gas and slurry phase polymerization, and there are some differences with reaction types. In gas phase polymerization, the melting point of IPP goes to a higher temperature with increasing addition amount of external electron donor. In the point of view of the relationship between the polymer melting point and molecular weight, it can be considered that the molecular weight of IPP will increase with an increasing addition amount of external electron donor. Also, when PEEB-to-TEAL mole ratios are in the range of 0–0.05, DSC curves show double peaks. This is due to rearrangement of polymer crystals with increasing temperature. This means that the IPP consists of two kinds of crystals, which have different melting points, respectively. Therefore, based on the fact that DSC curve patterns are affected by the molecular weight of polymer, these results are closely related with the change of polymer molecular weight by the addi-

tion of external electron donor, showing a larger peak at PEEB to TEAL equal to 0.03 than at PEEB to TEAL equal to 0 at the low temperature range. This is due to an increase of low isospecific sites, which produce IPPs of low molecular weight by the addition of a small amount of electron donor. This can be due rather to the active site transition than to producing new sites; in other words, it can be considered that atactic sites are transferred into low isospecific sites by the addition of small amounts of external electron donor. Meanwhile, when the PEEB-to-TEAL mole ratio is 0.05, the peak at low temperature is decreased and disappears at PEEB to TEAL equal to 0.1. From these results, it can be suggested that the low isospecific sites produced by the transition of atactic sites are transferred again into high isospecific sites, which produce IPP of high molecular weight when the PEEB-to-TEAL mole ratio is above 0.03. In contrast with gas phase polymerization, the IPP produced by slurry phase reaction shows an increase of low temperature peaks with decreasing melting points until PEEB to TEAL equals 0.05. When the PEEB-to-TEAL mole ratio is 0.1,

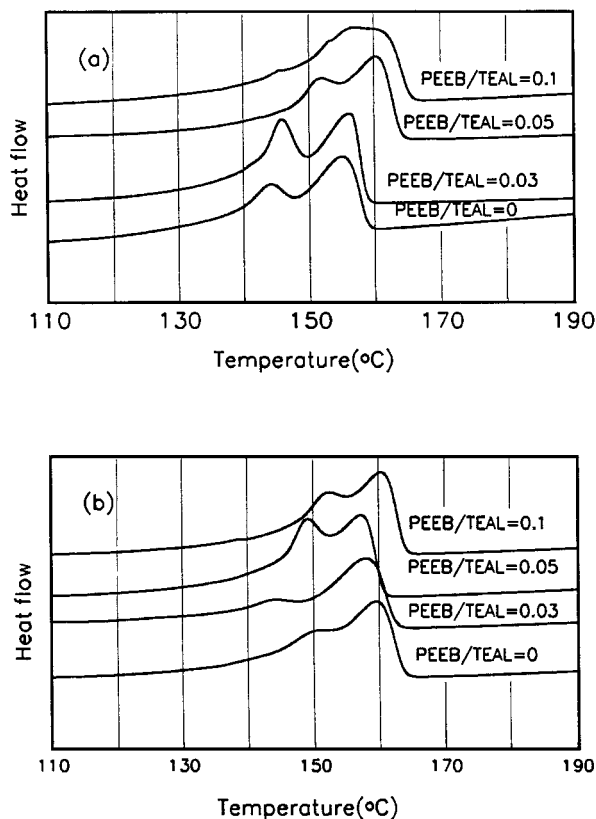


Figure 3 DSC curve patterns with the PEEB-to-TEAL mole ratio: (a) gas phase; (b) slurry phase.

the magnitude of the low temperature peak is decreased, and there is an increase of melting point. From these results, in slurry phase polymerization, the low isospecific sites from the transition of atactic sites increase until PEEB to TEAL equals 0.05, and then high isospecific sites increase due to the transition of low isospecific sites by more addition of external electron donor. Figure 4 shows the relationship between the PEEB-to-TEAL mole ratio and the melting point of IPP. As predicted in previous statements, sudden increases in melting point occurred at PEEB to TEAL equal to 0.03 in the gas phase and PEEB to TEAL equal to 0.05 in the slurry phase. Also, the melting points of IPP produced in the slurry phase show higher values than those of gas phase polymerization. These are due to the differences in polymerization types; in the slurry phase, much larger amounts of monomers are polymerized due to higher concentration than in the gas phase. From all of these results, it can be considered that there may be sudden changes in molecular weights of IPP because of the relationships between melting point and molecular weight, as discussed previously.

Molecular Weight Measurement by GPC

In practice, when molecular weight of isotactic polymer is measured by GPC, there are severe changes in the patterns of molecular weight distribution curves of isotactic PP with the changes of the PEEB-to-TEAL mole ratio, as shown in Fig-

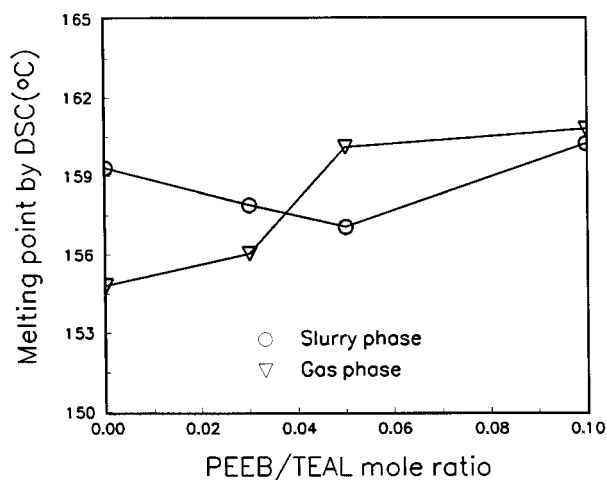


Figure 4 Changes of polymer melting point with the PEEB-to-TEAL mole ratio.

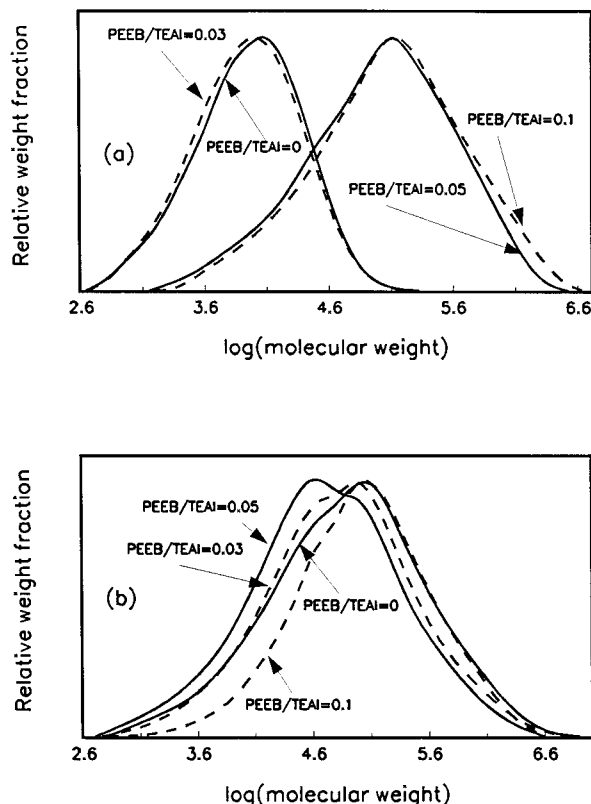


Figure 5 GPC curve patterns with the PEEB-to-TEAL mole ratio: (a) gas phase; (b) slurry phase.

ure 5. In the case of gas phase polymerization, molecular weight at PEEB to TEAL equal to 0.03 is shifted to a little lower region than that of PEEB to TEAL equal to 0. However, there is a large shift to higher molecular weight above PEEB to TEAL equal to 0.03. These results can not be explained by Keii's theory²; that is, atactic sites are selectively poisoned by the addition of electron donor, and molecular weight is increased by decreasing the cocatalyst amount, which has the function of chain transfer. However, it can be explained by active site transition phenomena, as discussed in the DSC results. That is, when an external electron donor is added to the catalyst, atactic sites are preferentially converted into low isospecific sites to a certain extent of added amount, and then converted into high isospecific sites above that amount. These are more definite in the slurry phase as shown in of Figure 5(b). Molecular weight is shifted lower until PEEB to TEAL equals 0.05, and then shifted higher again above PEEB to TEAL equal to 0.05. From these results, it can be considered that if the external electron donor is added to the catalyst first, atactic

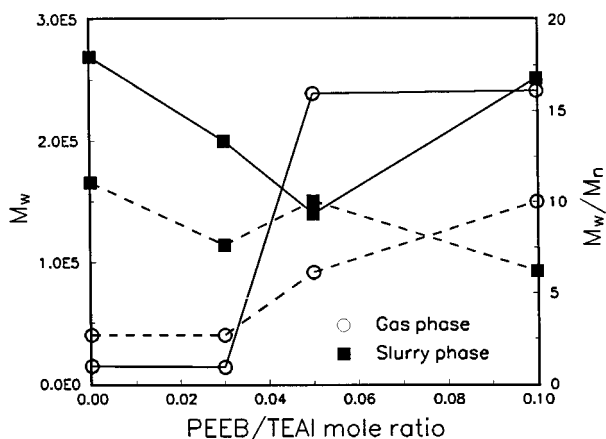


Figure 6 Relationship of M_w and $Q(M_w/M_n)$ with the PEEB-to-TEAL mole ratio: (—) M_w ; (.....) M_w/M_n .

sites are converted into low isospecific sites, which produce low-molecular-weight isotactic polymer. Second, low isospecific sites are converted into high isospecific sites, which produce high-molecular-weight isotactic polymer.

The weight-average molecular weight and molecular weight distribution (MWD) of IPP are compared between gas and slurry phase reactions in Figure 6. As previously mentioned for the GPC curves, weight-average molecular weight is increased remarkably over PEEB to TEAL equal to 0.03 in the gas phase. In the case of the slurry phase, molecular weight of IPP is decreased until PEEB to TEAL equals 0.05 because of atactic sites transition into low isospecific sites. However, it increases again above PEEB to TEAL equal to 0.05. And if atactic sites are selectively poisoned by electron donor, molecular weight distribution of IPP produced on the catalyst must not be changed because any changes do not happen on isotactic sites. However, the molecular weight distributions of IPP produced by both reactions have changed very significantly with the PEEB-to-TEAL mole ratio. This means that various active sites exist on the catalyst, and it strongly supports the active sites transition phenomena. Consequently, it is clearly proven that there are very close relationships between the melting point and the molecular weight of polymer. Meanwhile, relationships between polymer crystallinity and molecular weight are not found. These results can be explained by the fact that polymer crystallinities are only related to polymer tacticities, as suggested by Paukkeri and Lehtinen.¹⁵

Crystallization Patterns by Image Analyzer

In order to investigate the molecular weight of IPP indirectly, polymer crystallization patterns, such as formation of spherulites, were observed by an image analyzer. As shown in Figure 7, spherulites that consist of radial lamellae are formed at PEEB to TEAL equals 0 and become larger at PEEB to TEAL equals 0.03. These may be due to decreasing polymer molecular weight, as discussed in previous experiments, such as DSC and GPC; i.e., IPP of low molecular weight, which is composed of short polymer chains, can move freely in the melting state so that large spherulites can be formed more easily than for IPP of high molecular weight. Increased addition of external electron donor above PEEB to TEAL equals 0.05 does not show any spherulite formation. This may be due to producing IPP of very high molecular weight so they cannot rearrange to form spherulites easily. These results show good consistency with the results of GPC. In contrast with gas phase polymerization, spherulite are not formed until PEEB to TEAL equals 0.05 and disappear again at PEEB to TEAL equals 0.1 in the slurry phase reaction. The reasons for these phenomena are the same as for gas phase polymerization; also, they are very consistent with DSC and GPC results. Therefore, it can be concluded that crystallization patterns of the IPP polymer may be good proof to confirm the changes of polymer molecular weights. Consequently, all of these results clearly suggest that there may be active site transition with the addition of an external electron donor on Ziegler–Natta catalyst from the atactic site via the low isospecific site to the high isospecific site. The definite transitions of low isospecific site to high isospecific site are PEEB to TEAL equals 0.03 in the gas phase and PEEB to TEAL equals 0.05 in the slurry phase polymerization.

Results of UV VIS and FTIR Analysis

In order to investigate the reason for the active site transition phenomena, UV analysis was carried out for cocatalyst and electron donor polymerization additives. As shown in Figure 8, a peak at 254 nm corresponds to the electron donor and a peak at 227 nm corresponds to the cocatalyst. However, in the case of a mixture of them, a new peak at 214 nm appears. With the increasing PEEB-to-TEAL mole ratio, the 214 nm peak

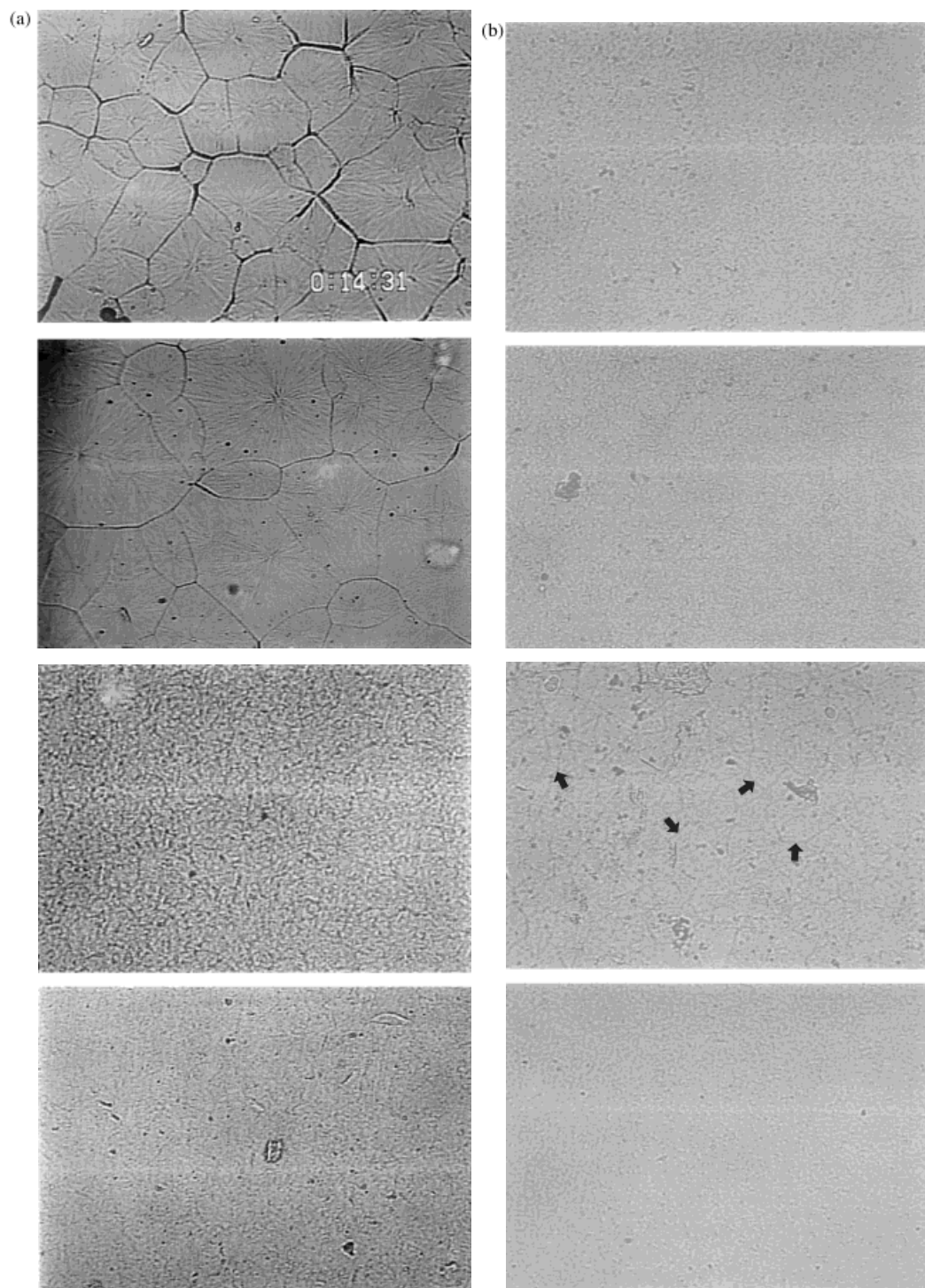


Figure 7 Photographs of PP crystalline: (a) gas phase in the order of PEEB to TEAL = 0, 0.03, 0.05, and 0.1; (b) slurry phase in the order of PEEB to TEAL = 0, 0.03, 0.05, and 0.1.

grows at the expense of the cocatalyst peak at 227 nm. From this result, it is found that a new complex is formed by mixing cocatalyst and electron donor, and all the cocatalyst is consumed to make up this complex. Therefore, it can be considered that this new complex has a function in catalyst active site transition from the atactic site to the isotactic site.

In another method to confirm the presence of this new complex, FTIR analysis was carried out; and the result is shown in Figure 9. Except for two peaks 1730.2 and 1279.8 cm^{-1} corresponding to the electron donor, a new peak at 1666.1 cm^{-1} is found, which is considered as a complex between cocatalyst and electron donor. Though it is difficult to assign this peak correctly, it may be a result of a C=O stretching mode in aromatic ketones.

CONCLUSIONS

Gas and slurry phase PP polymerizations were carried out respectively in CSBR, and various polymer characterization techniques were used to establish the function of an external electron do-

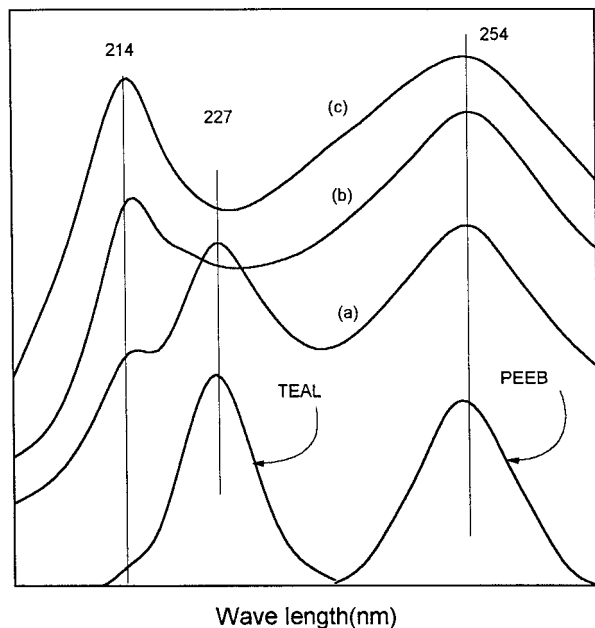


Figure 8 UV VIS spectra of PEEB, TEAL, and the PEEB-TEAL mixture with the PEEB-to-TEAL mole ratio: (a) PEEB to TEAL = 0.03; (b) PEEB to TEAL = 0.05; (c) PEEB to TEAL = 0.1.

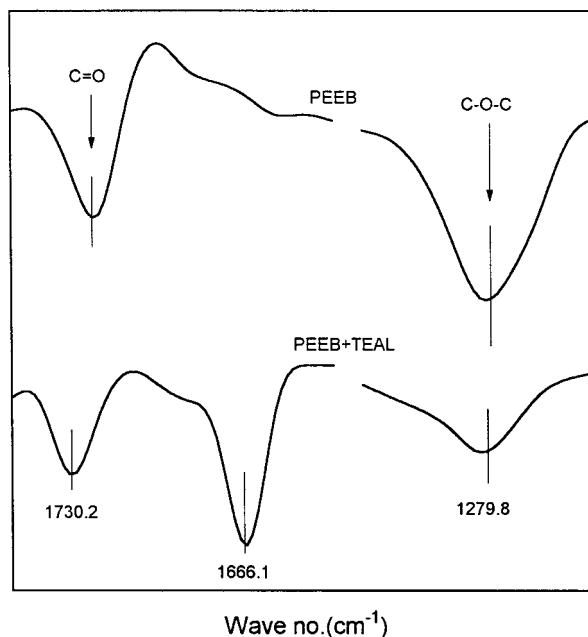


Figure 9 FTIR spectra of PEEB and the PEEB-TEAL mixture. PEEB to TEAL = 0.05.

nor on the third Ziegler-Natta catalyst, focusing on polymer molecular weight. From thermal analysis of the produced polymer, it was found that the external electron donor has a function in catalyst active site transition. The transition path is considered to be from the atactic site via the low isospecific site to the high isospecific site. There are some differences in the PEEB-to-TEAL mole ratio between gas and slurry phase for this transition; that is, PEEB to TEAL equals 0.03 in the gas phase, and PEEB to TEAL equals 0.05 in the slurry phase reaction. These may be due to differences in polymerization type. The results of GPC analysis show the same results with thermal analysis. Therefore, it is considered that there are close relationships between the polymer melting point and molecular weight. However, polymer crystallinity does not have any relationship with molecular weight. From another point of view, polymer crystalline formations, such as spherulite and lamella structures, were observed by image analysis and showed the same results as GPC. From these results, it is considered that polymer molecular weight can be predicted by observation of polymer crystalline form. From the results of UV VIS and FTIR experiments, some complexes are formed between cocatalyst and external electron donor, and it is considered that these complexes have a role in active site transition.

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