



Effects of polarizability and electronic character of phosphine ligand on the polymerization of 1,3-butadiene using Co-based catalyst

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Abstract

The effects of phosphine ligands on the polymerization of 1,3-butadiene with $\text{Co}(\text{2-ethyl hexanoate})_2/\text{AlEt}_2\text{Cl}/\text{H}_2\text{O}$ were investigated. Although the polarizability of phosphine ligands, i.e. the ratio of the average dipole moment to the molecular volume, had moderate impact on 1,4-*cis* stereoregularity, a good correlation was observed between polarizability and 1,4-*cis* stereoregularity regardless of the electronic character (π -acceptor or σ -donor) of phosphine ligands. On the other hand, neither catalytic activity nor the molecular weight (M_w) of polybutadiene showed a good correlation with polarizability. Catalytic activity was affected only when phosphine ligands were inordinately strong π -acceptors and σ -donors. High conversions of about 90% were obtained when phosphine ligands were moderate π -acceptors and σ -donors, regardless of their steric bulk. On the other hand, the electronic character of phosphine ligands significantly influenced the M_w of polybutadiene.

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1. Introduction

Controlling the stereoregularity of polybutadienes has attracted considerable attention in the rubber industry. The enhancement of stereoregularity, albeit on a small scale, is closely related to the improvement in the mechanical properties of polybutadiene such as tensile strength, heat build-up, and abrasion resistance [1–3]. Many organic and inorganic compounds are used to control stereoregularity leading to 1,4-*cis*-[4–6], 1,4-*trans*- [7], or 1,2-polybutadiene [8–11] with transition metal catalysts. However, few systematic

studies on the effect of phosphine ligands on the polymerization of 1,3-butadiene have been conducted. We recently reported the effects of phosphine ligand on the polymerization of 1,3-butadiene with a catalyst of $\text{Co}(\text{2-ethyl hexanoate})_2/\text{phosphine ligand}/\text{AlEt}_3/\text{H}_2\text{O}$ [12]. Both electronic and steric properties of phosphine ligands clearly affected stereoregularity and the molecular weight (M_w) of polybutadiene, while catalytic activity was influenced mainly by the steric bulk of phosphine ligands. Other representative examples of transition metal complexes containing phosphine ligands are $\text{Ni}(\text{acac})_2/\text{AlEt}_2\text{Cl}/\text{PPh}_3$ [13] and $\text{CoBr}_2 \cdot (\text{PPh}_3)_2/\text{Al}(i\text{-Bu})_3/\text{H}_2\text{O}$ [14], which provide 1,4-*cis*-1,4-*trans*-equibinary polybutadiene and polybutadiene with high 1,2-stereoregularity, respectively.

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We extended the study to a catalyst of $\text{Co}(\text{2-ethyl hexanoate})_2/\text{AlEt}_2\text{Cl}/\text{H}_2\text{O}$, which is one of the representative catalysts for the production of 1,4-*cis*-polybutadiene [15,16]. H_2O has been known as an indispensable ingredient for catalytic activity. We found that 1,4-*cis* stereoregularity, catalytic activity, and the M_w of polybutadiene were influenced by the nature of phosphine ligand. This paper reports the effects of phosphine ligand on the polymerization of 1,3-butadiene with $\text{Co}(\text{2-ethyl hexanoate})_2/\text{phosphine ligand}/\text{AlEt}_2\text{Cl}/\text{H}_2\text{O}$, and elucidates the factors that determine 1,4-*cis* stereoregularity, catalytic activity, and the M_w of polybutadiene.

2. Experimental

2.1. Materials

The following materials were purchased from Aldrich: triphenylphosphine (PPh_3), diphenyl(pentafluorophenyl)phosphine ($(\text{C}_6\text{F}_5)\text{PPh}_2$), bis(pentafluorophenyl)phenylphosphine ($(\text{C}_6\text{F}_5)_2\text{PPh}$), tris(pentafluorophenyl)phosphine ($\text{P}(\text{C}_6\text{F}_5)_3$), tris(2-methylphenyl)phosphine ($\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$), tris(2,4,6-trimethylphenyl)phosphine ($\text{P}[2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2]_3$), triisopropylphosphine ($\text{P}(\text{isopropyl})_3$), AlEt_2Cl , and $\text{Co}(\text{2-ethyl hexanoate})_2$. $\text{Co}(\text{2-ethyl hexanoate})_2$ was diluted to 0.1% (w/w) solution in CH_2Cl_2 , and the solution was stored in a crown-sealed bottle under nitrogen. All phosphine compounds were diluted to 0.5% (w/w) solution in toluene in crown-sealed bottles under nitrogen. AlEt_2Cl was used as received without dilution. The Yecheon plant of the Korea Kumho Petrochemical Co. supplied the 1,3-butadiene. The 1,3-butadiene was passed through a cylinder packed with activated alumina before it was used.

2.2. Polymerization

Polymerizations were performed in a 350 ml glass reactor purged with nitrogen. Benzene containing the desired amount of H_2O , 1,3-butadiene, $\text{Co}(\text{2-ethyl hexanoate})_2$, phosphine compound, and AlEt_2Cl were added sequentially to the reactor and the reaction was conducted at 40°C for 1 h. The resulting polybutadiene was stabilized with 2,6-di-*tert*-butyl-4-methylphenol and quenched with ethanol.

2.3. Characterization

Conversion was defined as the percentage by weight of the isolated polymer compared with the weight of the initially charged 1,3-butadiene. The microstructure of the polybutadiene was determined by taking IR spectroscopy (Bio-Rad, FTS 60-A) in CS_2 solution according to the literature [17]. Gel permeation chromatography data were obtained using a Viscotek TDA 300, employing connected Tosoh columns packed with polystyrene, G-6000-HXL, G-5000-HXL, G-4000-HXL, and G-3000-HXL, with a refractive index detector. THF was used as the eluent at a flow rate of 1.0 ml/min. Polystyrene standards with M_w in the range of 1050–5,000,000 were used for calibration.

3. Results and discussion

3.1. Effects of polarizability on 1,4-*cis* stereoregularity

The effects of phosphine ligand on 1,4-*cis* stereoregularity, catalytic activity, and the M_w of polybutadiene are shown in Table 1. According to Tolman's study [18,19], the electron density of the phosphorus atom will increase in the order of $\text{P}(\text{isopropyl})_3 > \text{P}[2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2]_3 > \text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3 > \text{PPh}_3 > (\text{C}_6\text{F}_5)\text{PPh}_2 > (\text{C}_6\text{F}_5)_2\text{PPh} > \text{P}(\text{C}_6\text{F}_5)_3$. The width of the cone angle, which is a measure of the steric bulk of phosphine ligand, will increase in the order of $\text{P}[2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2]_3 > \text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3 > \text{P}(\text{C}_6\text{F}_5)_3 > (\text{C}_6\text{F}_5)_2\text{PPh} > \text{P}(\text{isopropyl})_3 > (\text{C}_6\text{F}_5)\text{PPh}_2 > \text{PPh}_3$. PPh_3 has been known as a σ -donor [20]. On the other hand, $(\text{C}_6\text{F}_5)\text{PPh}_2$ can be considered as a π -acceptor based on the reports wherein PPh_2H , known to have more basic character than $(\text{C}_6\text{F}_5)\text{PPh}_2$, is realized to be a π -acceptor [18,20]. Thus, the three phosphine ligands, $(\text{C}_6\text{F}_5)\text{PPh}_2$, $(\text{C}_6\text{F}_5)_2\text{PPh}$, and $\text{P}(\text{C}_6\text{F}_5)_3$, apparently act as π -acceptors, while $\text{P}(\text{isopropyl})_3$, $\text{P}[2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2]_3$, $\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$, and PPh_3 as σ -donors. Phosphine ligands with three identical substituents such as $\text{P}(\text{C}_6\text{F}_5)_3$, PPh_3 , $\text{P}[2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2]_3$, and $\text{P}(\text{isopropyl})_3$ (but not $\text{P}(\text{2-CH}_3\text{C}_6\text{H}_4)_3$) provided polybutadienes with 1,4-*cis* contents more than 95%, regardless of their electronic character and steric bulk. On the other hand,

Table 1

Effects of phosphine ligands on the polymerization^a of 1,3-butadiene with a catalyst of Co(2-ethyl hexanoate)₂/AlEt₂Cl/H₂O

Entry	Phosphine ligand	Conversion (%)	Microstructure			M_w	M_w/M_n
			1,4- <i>cis</i> (%)	1,2-Polybutadiene (%)	1,4- <i>trans</i> (%)		
1	P(C ₆ F ₅) ₃	15.7	97.3	1.3	1.4	1272000	2.70
2	(C ₆ F ₅) ₂ PPh	97.3	91.1	2.9	6.0	714000	3.04
3	(C ₆ F ₅)PPh ₂	95.2	90.6	5.5	3.9	568000	3.40
4	PPh ₃	92.5	95.3	2.8	1.9	697000	3.10
5	P(2-CH ₃ C ₆ H ₄) ₃	89.5	87.0	8.2	4.8	374000	4.52
6	P[2,4,6-(CH ₃) ₃ C ₆ H ₂] ₃	87.5	95.1	2.4	2.5	1127000	3.29
7	P(isopropyl) ₃	42.5	98.0	1.1	0.9	2031000	2.01

^a Polymerization conditions: benzene/1,3-butadiene (w/w) = 6; [phosphine ligand]/[Co] = 2; [Al]/[Co] = 50; [H₂O]/[Co] = 20; concentration of Co per 100 g of 1,3-butadiene = 1×10^{-4} mol.

when one of the substituents was different from the other two such as (C₆F₅)₂PPh and (C₆F₅)PPh₂, the 1,4-*cis* contents decreased to about 91%. This showed that the identity of the three substituents on the phosphorus atom is an important factor directing 1,4-*cis* stereoregularity. The decrease in the 1,4-*cis* content obtained from P(2-CH₃C₆H₄)₃ was quite interesting, based on the results shown in entries 1, 4, 6 and 7; however, this showed another important factor directing stereoregularity to the 1,4-*cis* unit. Aside from the identity of the three substituents on the phosphorus atom, the symmetry of the P-R moiety appeared to be important for high 1,4-*cis* stereoregularity. The P-R moiety of P(C₆F₅)₃, PPh₃, P[2,4,6-(CH₃)₃C₆H₂]₃, and P(isopropyl)₃ had C_{2v} symmetry, which was lacking in the P-R moiety of P(2-CH₃C₆H₄)₃.

The effect of phosphine ligand on the 1,4-*cis* stereoregularity was not profound because the resultant polybutadienes had high 1,4-*cis* contents ranging from 87.0 to 98.0% (entries 1–7). Nonetheless, about 10% change in the 1,4-*cis* content could be considered meaningful to 1,4-*cis*-polybutadiene. The physical properties of 1,4-*cis*-polybutadiene such as tensile strength, heat build-up, and abrasion resistance greatly improved even with a slight increase in the 1,4-*cis* content, particularly for the 1,4-*cis* content of around 90% [1–3].

The main role of AlEt₂Cl in the Co-based catalyst is to reduce Co(II) to Co(I) followed by the oxidative addition of 1,3-butadiene through η^4 -*cis*-, η^4 -*trans*- or η^2 -*trans*-coordination to the Co(I) species, generating an active center, η^3 -Co(II)-allyl bond [21], at the last polymerized unit. The η^3 -Co(II)-allyl bond can exist in two isomeric forms, anti and syn, which are in

equilibrium, and it has two reactive sites, C₁ and C₃ [12,22–24]. The reaction of the incoming monomer at C₁ gives a 1,4-unit, which can be *cis* or *trans* depending on whether the allylic group is anti or syn, whereas the reaction at C₃ leads to a 1,2 unit independent of the structure of the allylic group. The predominant preference for the 1,4-*cis* unit observed for entries 1–7 seemed to be derived from a coordination intermediate with an η^4 -*cis*-coordination of monomer and an anti structure of the allylic group. Whether the degree of stereoregularity was imparted to 1,4-*cis* unit seemed to be determined by the effects of phosphine ligand on the active center.

The elucidation of the lowered 1,4-*cis* stereoregularity observed with (C₆F₅)₂PPh, (C₆F₅)PPh₂, and P(2-CH₃C₆H₄)₃ appeared to be quite difficult. However, the results observed for entries 1–7 led us to focus on the properties of phosphine ligands that would be affected by the identity of the three substituents and the symmetry of the P-R moiety. One of these properties was dipole moment. The Co(II) in the catalytic complex was expected to attract the negative end of the dipole of phosphine ligand and repel the positive end. Furthermore, there should be an induced ion-dipole interaction when phosphine ligand approached Co(II) due to the ionic character of Co and the dipole of phosphine ligand. The change in the polarized state of the Co orbital with variations in phosphine ligand was expected to affect the bond distances and the angles in the catalytic complex, thus influencing its geometry. Variations in the geometry of the catalytic complex would modify the position of the coordinated monomer with respect to the allylic group so as to make possible the formation of one rather than the other unit. In addition,

Table 2

The polarizability of phosphine ligand obtained from the ratio of average dipole moment to the molecular volume

Phosphine ligand	Average dipole moment (Debye)	Molecular volume (cm ³ /mol)	Polarizability ((Debye mol)/cm ³ , × 10 ⁻³)
P(C ₆ F ₅) ₃	0.5876	244.609	2.402
(C ₆ F ₅) ₂ PPh	3.4537	237.269	14.556
(C ₆ F ₅)PPh ₂	3.2766	208.743	15.697
PPh ₃	1.5826	197.347	8.019
P(2-CH ₃ C ₆ H ₄) ₃	0.5519	257.408	2.144
P[2,4,6-(CH ₃) ₃ C ₆ H ₂] ₃	0.7622	307.554	2.478
P(isopropyl) ₃	1.4655	149.747	9.787

the presence of a bulky phosphine ligand at the coordination site of active center was also expected to affect the geometry of the Co complex. Thus, the ratio of the average dipole moment to the molecular volume of phosphine ligand, i.e. polarizability [25], was a more precise expression than the dipole moment itself in stating accurately the effect of phosphine ligand on the active center. The average dipole moment and the molecular volume of phosphine ligand were obtained using the density functional theory method (B3PW91/6-31G) [26,27] and the results are shown in Table 2. The polarizability decreased in the order of (C₆F₅)PPh₂ > (C₆F₅)₂PPh > P(C₆F₅)₃ for phosphine ligands with π -acceptor character. (C₆F₅)PPh₂ gave polybutadiene with a 1,4-*cis* content of 90.6%; (C₆F₅)₂PPh and P(C₆F₅)₃ resulted in a 1,4-*cis* content of 91.1 and 97.3%, respectively. This clearly showed that the increase in polarizability lowers the 1,4-*cis* content for phosphine ligands with π -acceptor character (Fig. 1a). In contrast, higher 1,4-*cis* contents were obtained with an incremental increase in polarizability when phosphine ligand had σ -donor character (Fig. 1b). P(2-CH₃C₆H₄)₃ gave polybutadiene with a 1,4-*cis* content of 87.0%; PPh₃ and P(isopropyl)₃ gave a 1,4-*cis* content of 95.3 and 98.0%, respectively. P[2,4,6-(CH₃)₃C₆H₂]₃ was expected to have considerable difficulty in coordinating with Co due to steric bulkiness. This would explain the high 1,4-*cis* content of around 95% in spite of low polarizability. It has been reported that the polymerization performed with Co salt/AlEt₂Cl/H₂O in the absence of phosphine ligand gave 1,4-*cis* contents of 94–97% [28]. Evidently, 1,4-*cis* stereoregularity had a good correlation with polarizability regardless of the electronic character (π -acceptor or σ -donor) of phosphine ligands.

The vector sum of the three bond dipoles in phosphine ligand with π -acceptor character was a dipole with its positive end on the phosphorus atom, causing repulsion when it came close to Co. Lesser repulsion (dipole) resulted in greater variation in the geometry of the catalytic complex. On the other hand, the vector sum of the three bond dipoles in phosphine ligand with σ -donor character had its negative end on the phosphorus atom, causing attraction as it approached Co. This time, greater attraction (dipole) resulted in greater variation in the geometry of the catalytic complex. This showed how polarizability influenced 1,4-*cis* stereoregularity depending on the electronic character of the phosphine ligand. The higher 1,4-*cis* stereoregularity observed with the phosphine ligand with greater attraction to Co was ascribed to greater variation in the geometry, resulting in closer bonding distance between one terminal carbon atom of the incoming monomer and C₁ in the allylic group.

3.2. Effects of electronic character on catalytic activity

In contrast to 1,4-*cis* stereoregularity, catalytic activity did not show a general correlation with polarizability (Tables 1 and 2). (C₆F₅)₂PPh and (C₆F₅)PPh₂, which had greater polarizability than P(C₆F₅)₃, gave higher conversions than P(C₆F₅)₃. This seemed to show that polarizability had an effect on catalytic activity in polymerization using a phosphine ligand with π -acceptor character. However, no strong correlation was observed for a phosphine ligand with σ -donor character. There was no correlation between conversion and polarizability.

Indeed, catalytic activity was affected only when phosphine ligands were inordinately strong

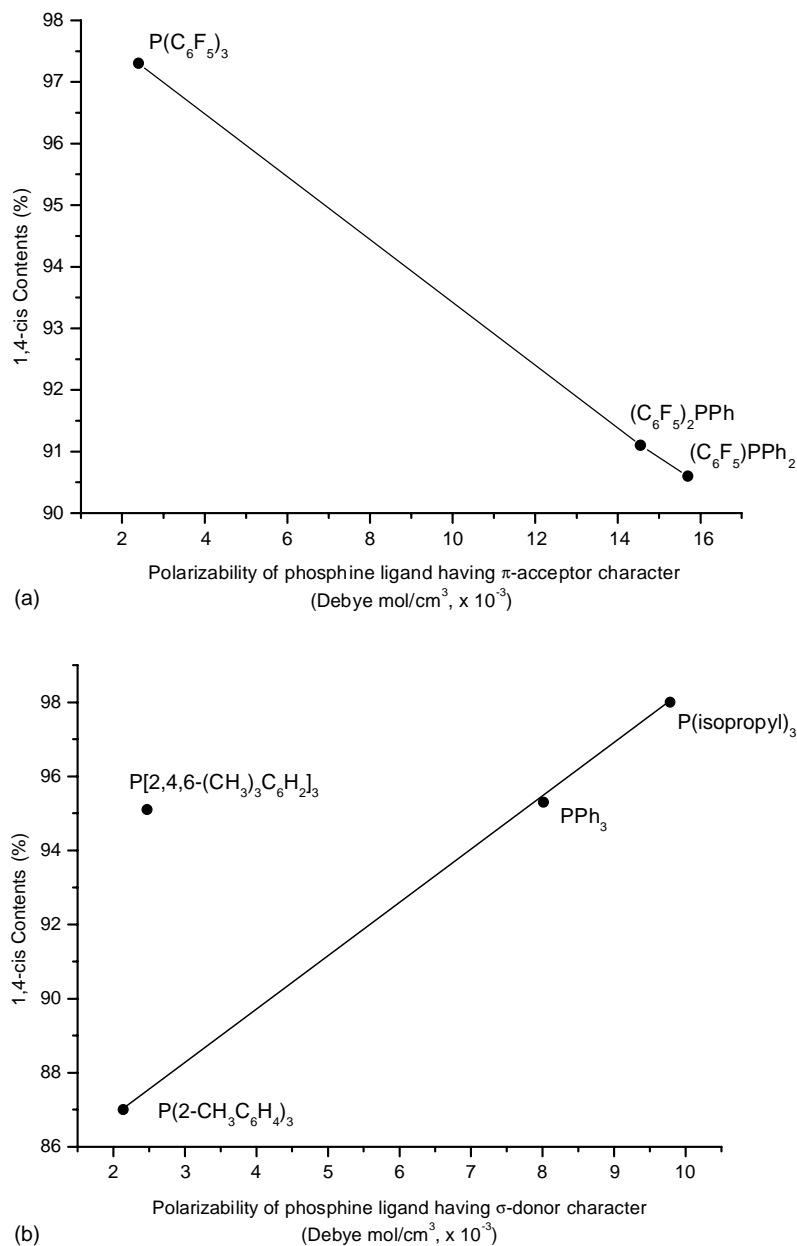


Fig. 1. The correlation between 1,4-*cis* stereoregularity and the polarizability of phosphine ligand having (a) π -acceptor and (b) σ -donor character.

π -acceptors and σ -donors. High conversions of about 90% were obtained when phosphine ligands were moderate π -acceptors and σ -donors regardless of their steric bulk (Fig. 2). The conversion, however, decreased significantly to below 50% when phos-

phine ligands were inordinately strong π -acceptors and σ -donors as observed with P(C₆F₅)₃ and P(isopropyl)₃, respectively.

It was still difficult to explain why polarizability did not have a general correlation with catalytic

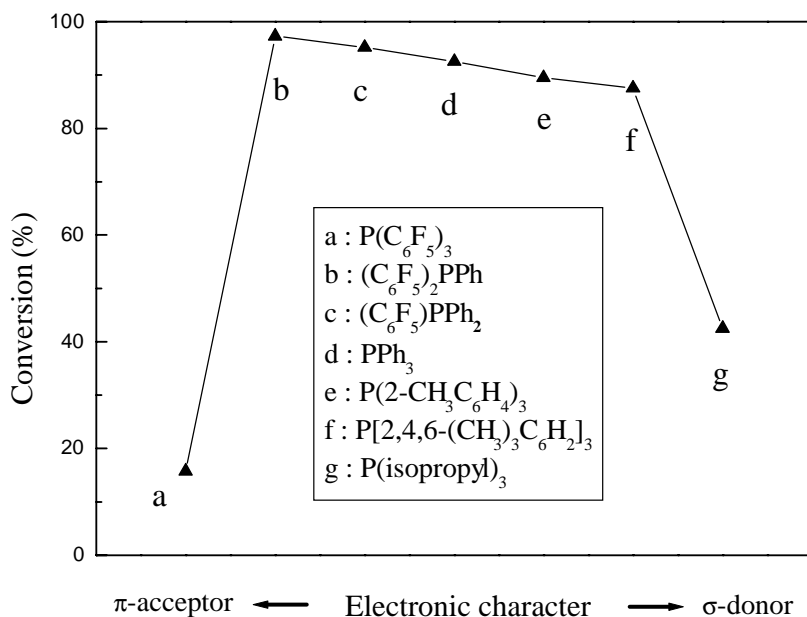


Fig. 2. Effects of the electronic character of phosphine ligand on the catalytic activity.

activity. However, the factors that might cause the inordinate intensity in electronic character to affect catalytic activity could be inferred. Conceivably, two forces are operating in opposite directions when the oxidation state of Co changes. The decrease in the oxidation number of Co decreases its electronegativity. This makes Co more polarized and consequently more able to insert the coordinated 1,3-butadiene. However, the progressive filling of Co orbitals with electrons should decrease the acceptor characteristic of Co for monomer, thus decreasing the ability of Co to coordinate with it. The converse of this mechanism should also be true. Thus, an appropriate balance of these two forces should be maintained to optimize catalytic activity. This could be the reason catalytic activity was affected mainly by the inordinate intensity in the electronic character of phosphine ligand.

3.3. Effects of electronic character on molecular weight (M_w)

The phosphine ligand had a very notable effect on the M_w of polybutadiene. $P(C_6F_5)_3$ gave polybutadiene with a M_w of around 1,272,000; $(C_6F_5)_2PPh$

and $(C_6F_5)PPh_2$ gave a M_w of around 714,000 and 568,000, respectively. The M_w of polybutadiene significantly increased with an increase in π -acceptor character and steric bulk of phosphine ligand in polymerization using a phosphine ligand with π -acceptor character (entries 1–3). However, to ascribe this significant increase in M_w to an increase in steric bulk could not be justifiable because the most sterically hindered phosphine ligand, $P[2,4,6-(CH_3)_3C_6H_2]_3$, did not give the largest M_w . Another example showing that the increase in M_w might originate from an electronic effect was seen in polymerizations using $(C_6F_5)_2PPh$ and $P(isopropyl)_3$. $(C_6F_5)_2PPh$ had a wider cone angle than $P(isopropyl)_3$. Nonetheless, $P(isopropyl)_3$ gave polybutadiene with a much higher M_w . This clearly showed that the increase in M_w observed in entries 1–3 was mainly from the electronic effect of phosphine ligand rather than its steric effect. Thus, it was plausible that the M_w of polybutadiene was primarily determined by the intensity in π -acceptor character in polymerization using a phosphine ligand with π -acceptor character. The chain transfer reaction seemed to take place more frequently with decreasing π -acceptor character of phosphine ligand (entries 1–3).

In contrast, the M_w of polybutadiene was mainly determined by the intensity in σ -donor character when using phosphine ligands with σ -donor character, such as PPh_3 , $\text{P}[2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2]_3$, and $\text{P}(\text{isopropyl})_3$. The M_w of polybutadiene increased with increasing intensity in σ -donor character of phosphine ligand. Its steric bulk showed little correlation with the M_w of polybutadiene. There may be other unidentified factors responsible for the deviation of the M_w of polybutadiene. The broadest molecular weight distribution (MWD) observed with $\text{P}(2\text{-CH}_3\text{C}_6\text{H}_4)_3$ in entry 5 showed that the ligand increased the heterogeneity of active centers.

The polarizability of phosphine ligand did not show a general correlation with the M_w of polybutadiene. The M_w of polybutadiene increased with decreasing polarizability when a phosphine ligand with π -acceptor character was used (Tables 1 and 2). However, no such clear correlation was observed for phosphine ligand with σ -donor character. Apparently, polarizability was not an appropriate parameter that could elucidate universally the effect of phosphine ligand on the M_w of polybutadiene.

4. Conclusions

The effects of phosphine ligands on the polymerization of 1,3-butadiene with $\text{Co}(2\text{-ethyl hexanoate})_2/\text{AlEt}_2\text{Cl}/\text{H}_2\text{O}$ were investigated. A good correlation was observed between polarizability and 1,4-*cis* stereoregularity regardless of the electronic character (π -acceptor or σ -donor) of phosphine ligands. On the other hand, neither catalytic activity nor the M_w of polybutadiene showed a good correlation with polarizability. Variations in polarizability provided polybutadienes with 1,4-*cis* contents ranging from 87.0 to 98.0%. The marked preference for a 1,4-*cis* unit seemed to be derived from a coordination intermediate with an η^4 -*cis*-coordination of monomer and an anti structure of the allylic group. Whether the stereoregularity was imparted to the 1,4-*cis* unit seemed to be determined by variations in the geometry of the catalytic complex. This was presumably caused by the difference in the polarizability of phosphine ligand. Catalytic activity was affected only when phosphine ligands were inordinately strong π -acceptors and σ -donors. High conversions of about 90% were

obtained when phosphine ligands were moderate π -acceptors and σ -donors regardless of their steric bulk. On the other hand, the electronic character of phosphine ligand significantly influenced the M_w of polybutadiene. In polymerization using a phosphine ligand with π -acceptor character, the M_w of polybutadiene was primarily dependent on the π -acceptor character rather than the steric bulk of phosphine ligand. The M_w of polybutadiene was mainly dependent on the σ -donor character of phosphine ligand when using a phosphine ligand with σ -donor character.

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