Electronic and Steric Effects of Phosphine Ligand on the Polymerization of 1,3-Butadiene Using Co-Based Catalyst

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Introduction

Stereoselective polymerization of 1,3-butadiene to 1,4-cis,[1] 1,4-trans,[1,2] or 1,2-polybutadiene[1,3,4] has been the subject of many studies. Many organic compounds, such as amines,[5,6] benzoquinones,[7,8] ethers,[9] halogenoacetic acids,[2,10] and phosphines,[11,12] are used to control stereoselectivity. Among these compounds, phosphines are the most attractive due to their electronic and steric properties. Several transition-metal complexes containing phosphine ligands are used as catalysts in the polymerization of 1,3-butadiene, but few systematic studies on the effect of phosphine ligands on the polymerization of 1,3-butadiene have been conducted. Representative examples of these complexes include $Ni(CO)_3 \cdot PPh_3/BF_3$,[13] $Ni(acac)_2/AlEt_2Cl/PPh_3$,[11] and $CoBr_2 \cdot (PPh_3)_2/Al(i\text{-}Bu)_3/H_2O$.[12,14] Of particular interest is the catalyst system of $CoBr_2 \cdot (PPh_3)_2/Al(i\text{-}Bu)_3/H_2O$, in which PPh_3 has been shown to be an indispensable ingredient for high 1,2-content and H_2O the key to catalytic activity.[12,14] On whole, this catalyst is known for its excellent activity, with 1,2-polybutadiene offering high processability.

We have examined recently the effects of phosphine ligands having different electronic and steric factors on the polymerization of 1,3-butadiene with Co(2-ethyl hexanoate)$_2$/$AlEt_3$/H_2O. We found that stereoregularity, catalytic activity, and the molecular weight (M_w) of polybutadiene were influenced significantly by the nature of the phosphine ligand. The present paper reports the electronic and steric effecs of the phosphine ligand on the polymerization of 1,3-butadiene and a plausible interpretation of this phenomenon, which is expected to provide a better understanding of the factors that determine stereoselectivity, catalytic activity, and the M_w of polybutadiene in the polymerization of 1,3-butadiene with Co salt/phosphine ligand/$AlEt_3$/H_2O.

Experimental Section

Materials. The following materials were purchased from Aldrich Chemicals: triphenylphosphine (PPh_3), biphenyl(pentafluorophenyl)phosphine ($(C_6F_5)PPh_2$), bis(pentafluorophenyl)phenylphosphine ($(C_6F_5)_2PPh$), tris(pentafluorophenyl)phosphine ($P(C_6F_5)_3$), tris(2,4,6-trimethylphenyl)phosphine ($P(2,4,6\text{-}[CH_3]_3C_6H_2)_3$), triisopropylphosphine (P(isopropyl)$_3$), $AlEt_3$, CH_2Cl_2, and Co(2-ethyl hexanoate)$_2$. Co(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 CH_2Cl_2 in crown-sealed bottles under nitrogen. 1,3-Butadiene was supplied by the Korea Kumho Petrochemical Co. from the Yeocheon plant. 1,3-Butadiene was passed through a tower of activated alumina before use.

Polymerization. Polymerizations were performed in a 350 mL glass reactor sufficiently purged with nitrogen. CH_2Cl_2 containing the desired amount of H_2O, 1,3-butadiene, Co(2-ethyl hexanoate)$_2$, phosphine compound, and $AlEt_3$ were added sequentially to the reactor and reacted at 10 °C for 5 h. The resulting polybutadiene was stabilized with 2,6-di-*tert*-butyl-4-methylphenol and quenched with ethanol.

Characterization. Conversion was calculated from 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 measured in CS_2 solution by IR spectroscopy (Bio-Rad, FTS 60-A) according to the literature.[15] The tacticity of the triad in the 1,2-unit was calculated by the peaks of the vinyl carbon appearing around 114 ppm in the ^{13}C NMR spectrum.[16] The ^{13}C NMR spectrum was obtained in $CDCl_3$ at room temperature with a Varian Unity Plus 400 spectrometer. Differential scanning calorimetry (DSC) was performed on the produced polymers with a Netzsch DSC-200 thermal analyzer at a heating rate of 10 °C/min. The crystallinity of the sample was determined by comparing the heat of fusion of the sample with the heat of fusion of a standard sample having 100% crystallinity.[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 solvent at a flow rate of 1.0 mL/min. Polystyrene standards in the 1050−5000 000 g/mol range were used for calibration.

Results and Discussion

Effects on the Stereoregularity. The effects of phosphine ligands on stereoregularity, catalytic activity, the M_w of polybutadiene, tacticity in 1,2-unit, and crystallinity are shown in Table 1. Polymerization using $(C_6F_5)PPh_2$ in entry 2 gave polybutadiene having somewhat lower 1,2-content than that of the polybutadiene produced using PPh_3 in entry 1, but 1,2-unit was still a major component in the microstructure, giving 85.9% of 1,2-content. A much more significant effect was observed in the polymerizations using $(C_6F_5)_2PPh$ in entry 3 and $P(C_6F_5)_3$ in entry 4, where 1,4-cis polybutadienes having 90.2% and 96.6% of 1,4-cis contents, respectively, were obtained. This shows that the nature of the phosphine ligand influenced significantly the active center, imparting stereoselectivity to either the 1,2- or 1,4-cis unit.

The mechanistic pathways for the formation of 1,2- and 1,4-cis units can be postulated as follows. Insertion of 1,3-butadiene through η^4-cis, η^4-trans, or η^2-trans coordination[18] into a Co−carbon bond, which is formed from the reaction of Co salt and $AlEt_3$, gives η^3-Co−allyl bond at the last polymerized unit. As shown in Figure 1, the η^3-Co−allyl bond can exist in two isomeric forms, anti and syn, which are in equilibrium, and it has two reactive sites, C_1 and C_3.[18−20] Reaction of the incoming monomer at C_1 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 C_3 leads to a 1,2-unit independent of the structure of the allylic group. The predominant preference for 1,2- and 1,4-cis units observed in entries 1−4 seems to derive from a coordination intermediate with an η^4-cis coordination of monomer and an anti structure of the allylic group. Whether stereoselectivity is imparted to either the 1,2- or 1,4-cis unit

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Table 1. Effects of Phosphine Ligands on the Polymerization[a] of 1,3-Butadiene with Co(2-ethyl hexanoate)$_2$/AlEt$_3$/H$_2$O

			microstructure					tacticity in 1,2-unit (%)			
entry	phosphine ligand	conv (%)	1,4-cis (%)	1,2 (%)	1,4-trans (%)	M_w	M_w/M_n	rr	mr	mm	crystallinity (%)
1	PPh$_3$	62.0	4.2	95.8	0.0	444 000	2.05	65.8	31.6	2.6	21.0
2	(C$_6$F$_5$)PPh$_2$	44.4	14.1	85.9	0.0	159 000	1.88	55.5	44.5	0.0	15.2
3	(C$_6$F$_5$)$_2$PPh	16.2	90.2	8.9	0.9	23 000	1.85	46.9	53.1	0.0	b
4	P(C$_6$F$_5$)$_3$	10.5	96.6	2.7	0.7	20 000	1.80	35.8	64.2	0.0	b
5	P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$	5.0	69.4	29.5	1.1	513 000	2.40	36.7	63.3	0.0	0.0
6	P(isopropyl)$_3$	24.0	1.8	98.2	0.0	465 000	2.08	25.6	45.8	28.6	0.0

[a] CH_2Cl_2/1,3-butadiene (wt/wt) = 6; [phosphine ligand]/[Co] = 2; [Al]/[Co] = 75; [H_2O]/[Co] = 50; concentration of Co per 100 g of 1,3-butadiene = 2×10^{-4} mol. [b] Measurement could not be performed due to waxy property.

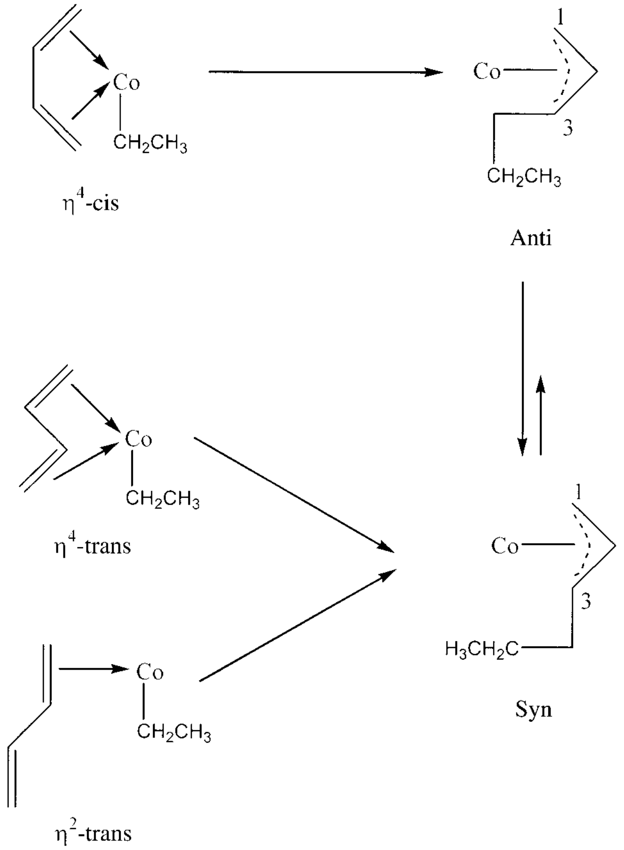

Figure 1. Formation of anti and syn forms of a η^3-Co−allyl bond at the last polymerized unit by the insertion of 1,3-butadiene through η^4-cis, η^4-trans, or η^2-trans coordination into a Co−carbon bond.

seems to be determined by the effects of the phosphine ligand on the active center.

The nature of the bond between Co metal and phosphorus might have a strong influence on the electron density of Co metal. Strong σ-donors will increase the electron density, whereas strong π-acceptors will decrease it.[21] The change in the electron density of Co metal with variations in the phosphine ligand is expected to affect the bond distances and the angles in the catalytic complex, thus influencing its geometry. It can be supposed that variations in the geometry of the catalytic complex, due to the type of phosphine ligand bonded to the metal, may 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. At present, however, ascertaining to what extent such modifications depend on the geometry of the catalytic complex is difficult, but the factors that might affect the geometry can be inferred. The presence of a bulky phosphine ligand at the coordination site of active center would affect the geometry of the Co complex. Thus, besides the electronic factor of the phosphine ligand, its steric factor is expected to cause preferential reaction of the incoming monomer either at C_1 or C_3 in the allylic group.

PPh$_3$ has been known as a σ-donor,[21] and (C$_6$F$_5$)PPh$_2$ can be considered as a π-acceptor.[21−23] The results obtained from PPh$_3$, (C$_6$F$_5$)PPh$_2$, (C$_6$F$_5$)$_2$PPh, and P(C$_6$F$_5$)$_3$ clearly show that 1,2-content increased with increasing σ-donor character (decreasing π-acceptor character) and decreasing steric bulk of the phosphine ligand, whereas 1,4-cis content increased as its π-acceptor character increased (σ-donor character decreased) and the steric bulk of the phosphine ligand grew. Thus, it can be inferred that the major geometry of the catalytic complex formed using either PPh$_3$ or (C$_6$F$_5$)PPh$_2$ should be such that one terminal carbon atom of the incoming monomer is at bonding distance from C_3 in the allylic group, but not from C_1. The converse of this mechanism should be true for the catalytic complex formed using either (C$_6$F$_5$)$_2$PPh or P(C$_6$F$_5$)$_3$.

The observation of high stereoselectivity imparted to either the 1,2- or 1,4-cis unit was further studied using P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ and P(isopropyl)$_3$ in entries 5 and 6, respectively. Tolman systematically parametrized electronic[22,24] and steric characteristics[22] of phosphine ligands. According to his study, the electron density of the phosphorus atom will increase in the order of P(isopropyl)$_3$ > P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ > PPh$_3$ > (C$_6$F$_5$)-PPh$_2$ > (C$_6$F$_5$)$_2$PPh > P(C$_6$F$_5$)$_3$; the width of the cone angle, which is a measure of the steric bulk of the phosphine ligand, will increase in the order of P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ > P(C$_6$F$_5$)$_3$ > (C$_6$F$_5$)$_2$PPh > P(isopropyl)$_3$ > (C$_6$F$_5$)PPh$_2$ > PPh$_3$. Thus, P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ can be considered a stronger σ-donor (weaker π-acceptor) and more sterically hindered than PPh$_3$. If only the electronic effect is considered, P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ is expected to yield polybutadiene having a higher 1,2-content, according to the results observed in entries 1−4, than that of the polybutadiene produced from PPh$_3$. However, it gave polybutadiene having a much lower 1,2-content, as observed. The huge steric bulk of P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ should cause an increase in 1,4-cis content at the expense of the 1,2-unit. To support this explanation P(isopropyl)$_3$, which has a much smaller steric bulk and a bit stronger σ-donor character than P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$,[22] was employed in entry 6. A dramatic increase in the 1,2-content to around 98% was observed. The decrease in steric bulk increased unambiguously the 1,2-content, although the possibility of some contribution from the fact that P(isopropyl)$_3$ is a bit stronger σ-donor (weaker π-acceptor) than P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ cannot be excluded. However, this does not mean that the steric effect is superior to the electronic impact in determining the chemoselectivity imparted to

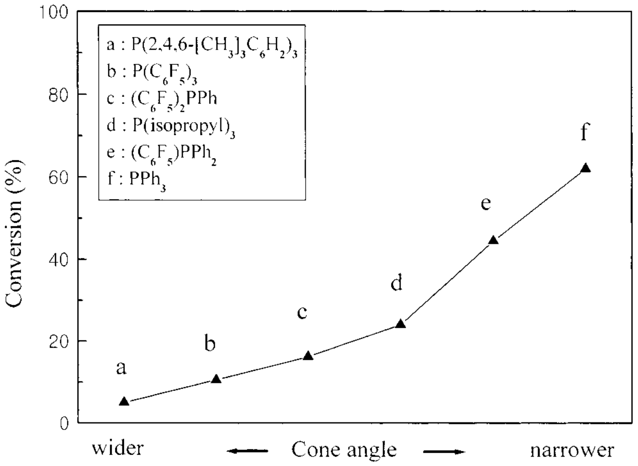

Figure 2. Dependence of the catalytic activity on the steric effect of the phosphine ligand.

either C_1 or C_3 in the allylic group. One good example showing the importance of the electronic effect on stereoselectivity can be seen in the polymerizations using $(C_6F_5)PPh_2$ and P(isopropyl)$_3$ in entries 2 and 6, respectively. The cone angle of P(isopropyl)$_3$ is wider than that of $(C_6F_5)PPh_2$.[22] Nonetheless, P(isopropyl)$_3$ gave a much higher 1,2-content, presumably due to its much stronger σ-donor character (weaker π-acceptor character). Thus, it seems that both the electronic and steric effects of the phosphine ligand are important in determining the preference of the reaction of the incoming monomer for either C_1 or C_3 in the allylic group.

The polybutadienes obtained using PPh_3 and $(C_6F_5)PPh_2$ had crystallinity in the range 15−25%, which is a typical range of crystallinity for the 1,2-polybutadienes produced with $CoBr_2{\cdot}(PPh_3)_2/Al(i\text{-}Bu)_3/H_2O$.[14] Those obtained using P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ and P(isopropyl)$_3$ were totally amorphous. The crystallinity observed in the polybutadienes obtained from PPh_3 and $(C_6F_5)PPh_2$ should be attributable to the syndiotactic arrangement of the 1,2-unit; the amorphism observed in the polybutadienes obtained using P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ and P(isopropyl)$_3$ should be caused, accordingly, by lower 1,2-content and the breakup of stereoregularity to syndiotactic and isotactic triads, respectively, as shown in Table 1. DSC could not be taken for the polybutadienes obtained from $(C_6F_5)_2PPh$ and $P(C_6F_5)_3$ due to their waxy properties.

Effects on the Catalytic Activity. An increase in congestion around the binding face of the active center is expected to affect catalytic activity. Higher conversion was obtained in the order of $PPh_3 > (C_6F_5)PPh_2 >$ P(isopropyl)$_3$ $> (C_6F_5)_2PPh > P(C_6F_5)_3 >$ P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ as shown in Figure 2. A decrease in the steric bulk of phosphine ligands, all the way from P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$ to PPh_3, increased catalytic activity irrespective of their intensity in π-acceptor or σ-donor character.

Effects on the Molecular Weight (M_w). The phosphine ligand had a very remarkable and complicated effect on the M_w of polybutadiene. PPh_3 gave polybutadiene having a M_w around 444 000; $(C_6F_5)PPh_2$, $(C_6F_5)_2PPh$, and $P(C_6F_5)_3$ gave a M_w around 159 000, 23 000, and 20 000, respectively. The M_w of polybutadiene significantly decreased with increasing π-acceptor character and steric bulk of the phosphine ligand. However, to ascribe this significant decrease in M_w to an incremental increase in steric bulk cannot be justifiable because the most sterically hindered phosphine ligand, P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$, gave the largest M_w, around 513 000. Another example showing that the decrease in M_w might originate from an electronic effect is seen in the polymerizations using $(C_6F_5)PPh_2$ and P(isopropyl)$_3$. P(isopropyl)$_3$ has a wider cone angle than $(C_6F_5)PPh_2$. Nonetheless, P(isopropyl)$_3$ gave polybutadiene having a much higher M_w. This clearly shows that the decrease in M_w observed in entries 1−4 arises mainly from the electronic effect of phosphine ligand rather than the steric effect. Thus, it is plausible that the M_w of polybutadiene was primarily determined by the intensity of π-acceptor character in the polymerization using the phosphine ligand having π-acceptor character. It seems that the chain transfer reaction takes place more frequently with increasing π-acceptor character of the phosphine ligand. On the other hand, the M_w of polybutadiene was mainly determined by the steric bulk of the phosphine ligand when using phosphine ligand having σ-donor character, such as PPh_3, P(2,4,6-[CH$_3$]$_3$C$_6$H$_2$)$_3$, and P(isopropyl)$_3$. The M_w of polybutadiene increased with increasing steric bulk of the phosphine ligand, and its intensity in σ-donor character did not show any correlation with the M_w of polybutadiene.

In summary, the tremendous effects of phosphine ligands on stereoregularity, catalytic activity, and the M_w of polybutadiene have been observed in the polymerization of 1,3-butadiene with Co(2-ethyl hexanoate)$_2$/$AlEt_3/H_2O$. The predominant preference for 1,2- and 1,4-cis units seems to derive from a coordination intermediate with an η^4-cis coordination of monomer and an anti structure of the allylic group. Whether stereoselectivity is imparted to either the 1,2- or 1,4-cis unit seems to be determined by variation in the geometry of the catalytic complex, presumably caused by electronic and steric effects of the phosphine ligand on the active center. Catalytic activity was mainly dependent on the steric bulk of the phosphine ligand. Lower conversion was obtained with increasing steric bulk of the phosphine ligand irrespective of its intensity in π-acceptor or σ-donor character. The phosphine ligand had a very remarkable and complicated effect on the M_w of polybutadiene. In the polymerization using a phosphine ligand having π-acceptor character, the M_w of polybutadiene was primarily dependent on the intensity of π-acceptor character rather than the steric bulk of the phosphine ligand. On the other hand, the M_w of polybutadiene was mainly dependent on the steric bulk of the phosphine ligand rather than its intensity in σ-donor character when using the phosphine ligand having σ-donor character.

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