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Synthesis of Regioblock Polybutadiene with $CoCl_2$-Based Catalyst via Reversible Coordination of Lewis Base

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Polybutadiene (PBD) is one of the most important polymers due to their extensive and diverse properties depending upon its microstructure. The development of homogeneous Ziegler−Natta catalysts has realized stereospecific polymerization of 1,3-butadiene to produce *cis*-1,4-, *trans*-1,4-, syndiotactic 1,2-, and isotactic 1,2-PBDs,[1] and the addition of Lewis bases plays a very important role in the control of the stereospecificity.[2−7] Among those catalysts, the addition of phosphines to Co-based catalysts was studied extensively for altering the regio- and/or stereospecificity of the active species because syndiotactic 1,2-PBD is commercially produced with those Co-based systems. The addition of phosphines to certain Co catalyst systems changed their stereospecificity from *cis*-1,4-specific to syndiotactic 1,2-specific.[3−5] The catalytic system composed of $CoX_2(PR_3)_2$ (X = Cl or Br) and methylaluminoxane (MAO) also produced PBDs enriched with syndiotactic 1,2 units.[6,7]

We have previously reported that *cis*-1,4 specific living polymerization of 1,3-butadiene proceeded with $CoCl_2-MAO$,[8] and the addition of a small amount (P/Co = 0.025 mol/mol) of triphenylphosphine (PPh_3) increased the incorporation of 1,2-unit to 14 mol % in the *cis*-1,4-PBD chain with keeping the livingness of the system.[4] The result indicates that one phosphine molecule interacted with multiple propagation centers. Therefore, if the interaction period between the phosphine and one propagation center is longer than the rate of monomer insertion, regioblock PBD should be formed in the present system. Further addition of PPh_3 increased the 1,2-content but caused chain transfer reaction. Although living polymerization is a powerful tool to synthesize block copolymers, one initiator (active species) is necessary for one polymer chain. The results of PPh_3 addition in $CoCl_2-MAO$ suggests that the system could catalytically give regioblock PBD.

We actually confirmed that 1,2- and 1,4-units were present blocky in the PBD chain through the hydrogenation of the PBD (HPBD). This Communication reports the preliminary results of the catalytic production of the regioblock PBDs with $CoCl_2$-modified MAO (MMAO) in the presence of phosphines.

The polymerization results of 1,3-butadiene by means of $CoCl_2-MMAO$ in the presence of PPh_3 or cyclohexyldiphenylphosphine ($PCyPh_2$) with various P/Co ratios are shown in Table 1. In both catalytic systems, the conversions increased according to the P/Co ratio, but the number-average molecular weights of the polymers obtained were almost the same with molecular weight distributions of ∼2. The results indicate that the chain transfer rate as well as the propagation rate was enhanced by the phosphines added.

The increase of P/Co ratio increased the content of 1,2-unit, and the polymers obtained in the presence of phosphines showed the melting point (T_m) even at the low 1,2-content of 24%, suggesting the blocky structure of 1,2-units. The stereoregularities of 1,2-sequences of PBDs with high 1,2-content were determined by ^{13}C NMR to be syndiotactic: syndiotactic triad (rr) was 58% in the presence of PPh_3 (entry 3) and 87% in the presence of $PCyPh_2$ (entry 5, Figure 1a). The higher T_m of PBD with $PCyPh_2$ is therefore ascribed to higher syndiotactic 1,2-PBD sequence, and the almost constant T_m values of ∼110 °C regardless of the 1,2-content suggest the presence of syndiotactic 1,2-block sequences. Ricci et al. investigated the effect of phosphine in the butadiene polymerization with the isolated complex, $CoCl_2(PRPh_2)_2$ (R = Me, Et, ^{n}Pr, ^{i}Pr, Cy), combined with MAO. They reported that P^iPrPh_2 and $PCyPh_2$ gave crystalline polymers with T_m values from 109 to 139 °C depending on the polymerization conditions, whereas the other less bulky $PRPh_2$ (R = Me, Et, ^{n}Pr) gave amorphous polymers.[7c]

The microstructures of PBDs were then analyzed in more detail by ^{13}C NMR after hydrogenation. As an example, the ^{13}C NMR spectrum of HPBD containing 71% of 1,2-unit obtained with $PCyPh_2$ is shown in Figure 1b, where the structure of HPBD and the peak assignments are also displayed. Tetramethylene unit derived from 1,4-addition and 1-butene unit derived from 1,2-addition are denoted C and V, respectively. The sequence distributions of C and V were determined from the spectra of the HPBD and are summarized in Table 2. The χ parameter that represents the block tendency of 1,2- and 1,4-addition is in the range of 0.27−0.60, which indicates the blocky structure of the PBDs regardless of the 1,2-content and the phosphine used. The number-average sequence lengths of 1,4- and 1,2-units of the PBDs with the similar 1,2-contents were larger in the presence of $PCyPh_2$ than in the presence of PPh_3. The results indicate that the regioblock structure of PBDs obtained with $CoCl_2-MMAO$ can be controlled with the kind and the amount of phosphine used. To the best of our knowledge, this is the first example for the characterization of regioblock PBDs.

The thermal properties of the HPBDs were determined by DSC. The HPBDs showed T_m, of which value decreased with increasing the 1,2-unit accompanied by the decrease of melting enthalpy (ΔH), indicating that the T_m is ascribed to long polymethylene sequence (Table 2). The results also testify the formation of the regioblock PBDs composed of rubbery *cis*-1,4-block and crystalline *syn*-1,2-block sequences in this catalytic system. For comparison, the PBD with similar 1,2-content was prepared with BuLi in heptane in the presence of THF and analyzed after hydrogenation (entry 6, Table 2). The results indicate that the 1,2- and 1,4-units are randomly distributed in the polymer obtained with BuLi.

The production of regioblock PBDs with $CoCl_2-MMAO-$phosphine can be explained by Scheme 1, where phosphine-free Co species (Co^+) and phosphine-coordinated Co species ($P-Co^+$) produce *cis*-1,4- and *syn*-1,2-PBD, respectively. Phosphine molecules should transfer between the propagation centers during polymerization at a longer interval than the rate of monomer insertion to give regioblock PBD.

In conclusion, we confirmed the regioblock structure of the PBDs obtained with $CoCl_2-MMAO-$phosphine (PPh_3 or $PCyPh_2$) by means of the ^{13}C NMR and DSC analysis of PBDs before and after hydrogenation. The results indicate that the systems are useful for the catalytic synthesis of regioblock PBDs composed of rubbery *cis*-1,4-block and crystalline *syn*-1,2-block

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Table 1. Results of 1,3-Butadiene Polymerization with $CoCl_2$−MMAO−Phosphine[a]

entry	phosphine	P/Co	conv. (%)	M_n[b] ($\times 10^4$)	M_w/M_n[b]	N[c] (μmol)	*cis*-1,4[d] (%)	1, 2[d] (%)	T_m[e] (°C)	T_g[e] (°C)	rr[f] (%)
1		0	19.5	16.7	1.6	3	98	2.0	[g]	[g]	
2	PPh_3	0.1	25.4	10.1	1.7	7	76	24	51	[g]	
3	PPh_3	0.5	37.0	11.9	2.3	8	29	71	67	−41	58
4	$PCyPh_2$	0.2	24.8	18.6	1.8	4	73	27	109	[g]	
5	$PCyPh_2$	0.5	59.4	17.2	2.0	9	29	71	113	−19	87

[a] Polymerization conditions: Al/Co = 600; TMA/Co = 5; $CoCl_2$, 6 μmol; butadiene, 2.7 g; toluene + monomer = 30 mL; temperature = 25 °C, time = 30 min. [b] Measured by GPC calibrated using polystyrene standard. [c] Number of polymer chains calculated from polymer yield and M_n. [d] Determined by ^{1}H NMR and ^{13}C NMR. [e] Determined by DSC. [f] Syndiotactic triad of 1,2-sequence determined by ^{13}C NMR. [g] Not detected.

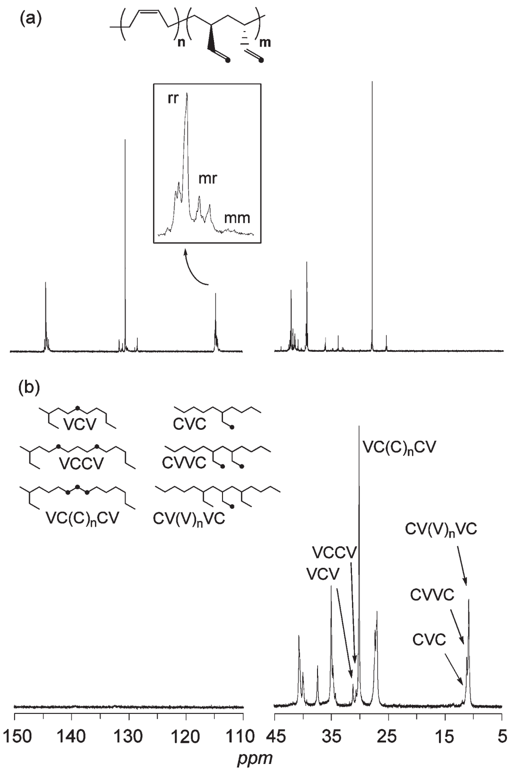


Figure 1. ^{13}C NMR spectra of PBD (entry 5) before and after hydrogenation: (a) PBD; (b) HPBD.

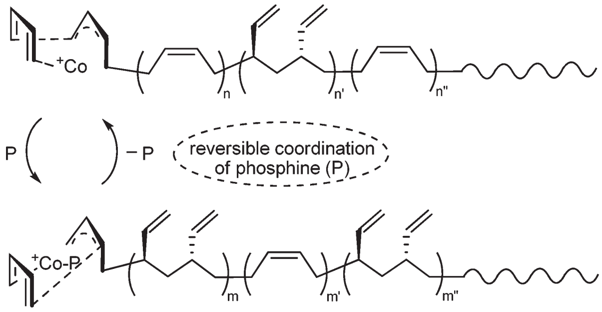
Table 2. Characterization of Hydrogenated Polybutadienes

entry	[VV]	[VC]	[CC]	χ[a]	$\bar{l}_V$[b]	$\bar{l}_C$[b]	T_m[c] (°C)	ΔH[c] (mJ/mg)
2	0.16	0.13	0.71	0.38	3	12	119	101
3	0.55	0.26	0.19	0.60	5	2	100	26
4	0.20	0.10	0.70	0.27	5	15	119	103
5	0.60	0.19	0.21	0.45	7	3	114	18
6	0.37	0.52	0.11	1.11	2	1	[d]	[d]

[a] χ parameter represent block tendency calculated by [VC]/2([V]·[C]). [b] Number-average length of each sequence. [c] Determined by DSC. [d] Not detected.

sequences via reversible coordination of phosphine to the active species, where the syndiotacticity of 1,2-block sequence and the sequence lengths of 1,2- and 1,4-units are controllable by selecting the kind and the amount of phosphine used.

Scheme 1. Proposed Mechanism for Formation of Regioblock PBD via Reversible Coordination of Phosphine



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Supporting Information Available: Experimental procedures, ^{13}C NMR spectra of PBDs, DSC profiles of PBDs and HPBDs, and polymerization results of 1,3-butadiene with BuLi. This material is available free of charge via the Internet at http://pubs.acs.org.

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