1,3-Butadiene Polymerization by Bis(benzimidazolyl)amine Metal Complexes: Remarkable Microstructural Control and a Protocol for In-Reactor Blending of *trans*-1,4-, *cis*-1,4-, and *cis*-1,4-*co*-1,2-Vinylpolybutadiene

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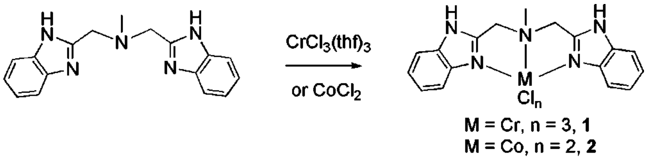
Polybutadiene (PBD) is a material that finds extensive and diverse applications, ranging from rubber tire manufacture through to hard coatings for golf balls.[1,2] Its properties are highly dependent upon the microstructure of the polymer backbone which can range from highly *cis*-1,4 (soft, rubbery) to highly *trans*-1,4 (hard) through to *cis* or *trans* structures that contain a significant proportion of pendant vinyl groups (*vinyl*-1,2).[2−4] The latter are particularly useful in providing cross-linking sites. While uses of polymer composite materials based on *cis*-1,4-polybutadiene and other polymers are well documented, applications of polymer blends containing *cis*-1,4-polybutadiene and *trans*-1,4-polybutadiene remain to be developed, a situation that may be rectified by in-reactor blending approaches of the type described here.[5]

Recently, we introduced a new family of olefin oligomerization and polymerization catalysts based on metal complexes stabilized by tridentate benzimidazolyl-containing ligands.[6,7] Here we describe the use of chromium and cobalt derivatives to polymerize butadiene with remarkable and contrasting selectivities and an in situ reactor blending protocol that allows the production of polymer mixtures consisting of *cis*-1,4, *trans*-1,4 and *vinyl*-1,2 microstructures.

The chromium and cobalt precatalysts **1** and **2** are readily prepared by treatment of $CrCl_3(thf)_3$ and $CoCl_2$ with bis-(benzimidazol-2-yl)methylamine (Scheme 1). The molecular structure of **1** (Figure 1) was determined and revealed a facial coordination of the bis(benzimidazol-2-yl)methylamine ligand with a Cr−N(amine) bond distance [2.190(4) Å] significantly longer than the Cr−N(benzimidazole) [2.023(4), 2.058(4) Å] bond lengths. The bond distances however are unexceptional and comparable to those in analogous complexes.[8] The X-ray structure of its cobalt relative **2** has been reported previously.[8]

Treatment of **1**/MAO with 1,3-butadiene in a Schlenk vessel afforded high conversion to polybutadiene over a period of 3 h. The yield was found to be dependent upon the MAO loading, with the highest conversion arising from a Cr:MAO ratio of 1:6000. The molecular weights of the resultant PBD were found to be in the range (74−109) × 10^3 g/mol, all with narrow molecular weight distributions (2.0−2.2), indicative of single-site catalyst behavior.

Scheme 1. Synthesis of Complexes 1 and 2



Monitoring the reaction over time revealed a linear increase in yield and a fairly constant catalyst turnover frequency (TOF) of 4938−5333 h^{-1}, after the first hour of the reaction, implying a constant concentration of the active species following the initiation period. The TOF could be raised to 137 000 h^{-1} by carrying out the polymerization at 50 °C in a 600 mL Parr reactor equipped with an efficient stirrer. This activity is considerably higher than for other metal-catalyzed butadiene polymerizations. A linear plot of $[BD]_t$ vs time (Supporting Information) is consistent with a zeroth-order dependence of the reaction on butadiene concentration, suggesting that the catalyst resting state during chain propagation likely has butadiene bound to the metal center. The molecular weight of the resultant PBD remained unchanged over the course of the polymerization, while the number of chains per Cr center increased, indicating a steady, controlled chain transfer process (see Supporting Information). The microstructure of the PBD was found to be ~99% *trans*-1,4 by NMR and IR spectroscopies (see Supporting Information), the remaining 1−2% being attributable to isolated *cis*-1,4 units.

For the cobalt catalyst, **2**, activated by MAO, a highly *cis*-1,4 microstructure (~97%) was obtained with molecular weights for the resultant PBD in the range (560−720) × 10^3 g/mol, somewhat higher than for the Cr system (Table 1). Encouraged by these observations of contrasting microstructural control using Cr and Co (benzimidazolyl)amine) complexes, we decided to investigate the possibility for in-reactor blending of the highly *cis*- and *trans*-PBD forms since postreactor blending of these materials is challenged due to their quite different physical properties. Satisfyingly, varying the proportions of Cr and Co catalysts in a dual-catalyst system allowed the *cis/trans* content to be varied in a systematic way (Figure 2), and an intimate blend of the two polymers could be isolated. DSC and ^{1}H DOSY analyses were carried out in order to confirm that the product was a mixture of *trans*- and *cis*-PBD rather than a diblock copolymer. DSC analysis shows melting points attributable to both the *cis* and *trans* polymers, while the ^{1}H DOSY

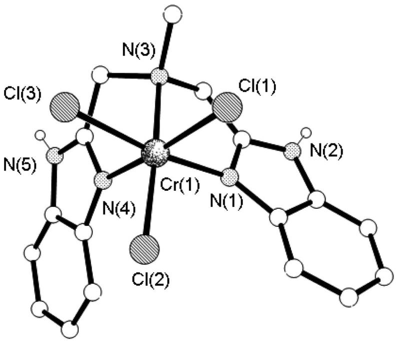


Figure 1. Molecular structure of **1**.

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Table 1. 1,3-Butadiene Polymerizations Using 1 and 2[a]

run	cat.	*t* (h)	Al/M (equiv)	PPh_3/M (equiv)	TOF (h^{-1})	conv (%)	microstructure[b] (mol %) *trans*-1,4-	*cis*-1,4-	1,2-	M_n (g/mol)	M_w/M_n
1	**1**	0.5	6000		2593	7.1	99	1	0	88 500	2.1
2	**1**	1.0	6000		4000	22.0	99	1	0	108 700	2.2
3	**1**	1.5	6000		4938	40.7	99	1	0	86 000	2.0
4	**1**	2.0	6000		5000	54.9	99	1	0	74 800	2.2
5	**1**	2.5	6000		5333	73.3	99	1	0	95 000	2.2
6	**2**	3.0	200		450	33.8	1	97	2	562 500	1.8
7	**2**	3.0	600		678	50.9	1	97	2	606 500	1.8
8	**2**	3.0	1000		493	37.0	1	97	2	719 000	1.7
9	**2**	1.0	600	0.2	260	14.3	2	88	10	112 900	2.0
10	**2**	1.0	600	0.6	260	14.3	6	61	33	96 000	1.8
11	**2**	1.0	600	1.0	370	20.3	4	31	65	102 000	1.9

[a] General conditions: glass Schlenk reactor under magnetic stirring, room temperature; precat: (**1**) = 0.5 μmol, (**2**) = 5 μmol; MAO cocat.: 1.6 M; BD_0 = 0.49 g from a toluene solution of 1,3-butadiene of 0.049 g/mL (runs 1−5 and 9−11) and 1.08 g from a toluene solution of 1,3-butadiene of 0.108 g/mL (runs 6−8); control experiments were carried out using MAO/toluene and $CrCl_3(THF)_3$ or $CoCl_2$. [b] Determined by ^{13}C NMR and FT-IR.

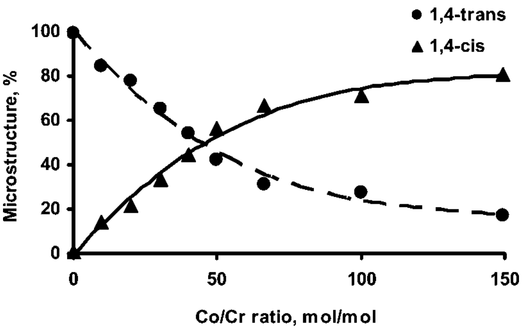

Figure 2. In-reactor blending of *cis*- and *trans*-PBD.

spectrum shows two different diffusion coefficients indicating the presence of two separate polymers. These findings are additionally supported by bimodal GPC traces for the *cis*-1,4- and *trans*-1,4-polybutadiene blends prepared at different initial monomer concentrations (see Supporting Information).

Extending this approach, it is known that addition of PPh_3 to cobalt butadiene polymerization catalysts can result in a significant proportion of *vinyl*-1,2 linkages which provide useful cross-linking sites in PBD materials.[4,9] **2**/MAO was found to respond in a similar manner, affording 33% 1,2-vinyl content at 0.6 equiv of PPh_3 and increasing to 65% 1,2-vinyl content at 1.0 equiv of added phosphine (Table 1). Contrastingly, treatment of a mixture of **1**/MAO with PPh_3 did not affect the catalyst activity nor the polymer microstructure. Thus, polymerization of 1,3-butadiene by a mixture of **1**/MAO, **2**/MAO, and PPh_3 resulted in the formation of blends of polybutadiene polymers containing *trans*-1,4-, *cis*-1,4-, and 1,2-vinyl linkages. It proved possible to vary the proportions of these microstructures by appropriate adjustment of the Cr:Co:PPh_3 ratio.

In conclusion, treatment of bis(benzimidazol-2-yl)methylamine complexes of Cr and Co results in the formation of very active catalysts for 1,3-butadiene polymerization. The polymer microstructure can be controlled by varying the active metal or using additives as PPh_3.

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Supporting Information Available: Experimental and spectroscopic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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