Polymerization and Copolymerization of Olefins and Acrylates by Bis(benzimidazole) Copper Catalysts

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Received April 28, 2003 Revised Manuscript Received September 4, 2003

There has been considerable recent activity in the area of late transition metal polymerization catalysis.^{1,2} In the past two decades, metallocenes have revolutionized the commercial polymerization of olefins. In many cases, these catalysts are now used in place of traditional Ziegler-Natta catalysts to produce better performing HDPE and LLDPE. Metallocenes are based on early transition metals, predominantly Ti, Zr, and Hf. These metals are very oxophilic and are very easily poisoned by polar monomers and contaminants.³ Catalysts with the ability to incorporate polar monomers may give rise to new high-performance materials with high adhesive, toughness, and dyability.⁴ These catalysts may also be more tolerant of minor contaminants in ethylene polymerization. The search for these types of polymerization catalysts has led to the late transition metals.

The copolymerization of olefins with acrylate monomers by organometallic catalysts has been an elusive goal. Late transition metal catalysts, in general, are less sensitive to deactivation by polar species than metallocenes. However, the known late metal catalysts still have difficulty preparing acrylate homopolymers and/ or in-chain olefin/acrylate copolymers. For example, the salicylaldimine-ligated "neutral nickel" catalysts reported by Grubbs⁵ only copolymerize ethylene with functional monomers in which a spacer group separates the functionality and the reactive double bond. Brookhart's early cationic Pd and Ni diimine catalysts⁶ can produce only low acrylate content ethylene copolymers (<20 mol %), which have the acrylate group at the ends of branches rather than in the polymer backbone chain. More recent versions⁷ of the Ni diimine catalysts are able to make in-chain copolymers, but they tend to be low molecular weight materials with low incorporation of polar monomers (<1.4 mol %). Similarly, Drent's⁸ recently reported [P,O]-ligated Pd catalysts also tend to produce low molecular weight, low acrylate content copolymers.

With the exclusion of ATRP (atom transfer radical polymerization) catalysts, which have been reported for many transition metals, polymerization catalysts based on copper are considerably rare. One rather ambiguous example has been reported.⁹ One other example is Shibayama's¹⁰ aminidate-ligated Cu catalyst system; however, only homopolymers have been reported with these initiators. Cu ATRP catalysts can be exemplified by the pioneering work of Matyjaszewki¹¹ and more recently of Sen.¹² However, these systems are free radical initiators, albeit living radical ones. Free radical

Scheme 1. Synthetic Scheme for the Preparation of Bis(benzimidazole) Copper(II) Complexes 5–7



initiators do not readily homopolymerize ethylene under low-pressure, low-temperature conditions.

We have discovered that certain bis(benzimidazole)ligated Cu precatalysts (activated by MAO) not only homopolymerize both ethylene and various acrylates but also copolymerize these two monomer classes.¹³ These copper-based catalysts produce very highly linear polyethylene as well as incorporate certain α -olefins.¹⁴ Unlike conventional Brookhart Pd diimine-catalyzed ethylene/acrylate copolymers, the Cu-catalyzed copolymers are in-chain copolymers with high levels of acrylate incorporation, and a range of low to high molecular weight products have been prepared. This paper details the Cu bis(benzimidazole) (CuBBIM)/MAO-catalyzed homo- and copolymerizations of ethylene and alkyl (meth)acrylates and the characterization of the products formed from these systems.

These copper complexes are prepared in three synthetic steps as illustrated in Scheme 1. The first step is the acid-catalyzed condensation reaction of a dicarboxylic acid in acid with 2 equiv of phenylenediamine. Condensation of tartronic acid yields the carbinol-bridged bis(benzimidazole), 1a (X = -CHOH-). Condensation of malonic acid yields the methylene-bridged bis(benzimidazole), $\mathbf{1b}^{15}$ (X = $-CH_2-$). Condensation of diphenic acid yields the 2,2'-biphenyl-bridged bis-(benzimidazole), $1c^{16}$ (X = 2,2'-biphenyl). The next synthetic step is alkylation of the bis(benzimidazole). Compound **1a** can be alkylated sequentially up to four times, once each at the protonated nitrogens, followed by the carbinol and finally at the bridgehead carbon. Compound 1b can be alkylated sequentially up to four times, once each at the protonated nitrogens and twice at the methylene bridgehead carbon. In this study 1b was alkylated three times. Compound 1c was alkylated twice, once at each protonated nitrogen, (4a, 17, 4b). Finally, the alkylated bis(benzimidazole)s are metalated using CuCl₂·2H₂O in a mixture of ethanol and triethyl orthoformate (TEOF). Triethyl orthoformate is added to effect the dehydration of the reaction mixture and aid in the crystallization of the metal complex. The solid crystalline complexes are then isolated by filtration. Figure 1 shows an X-ray (ORTEP) structure for 5.18



Figure 1. Molecular structure of 5. Selected bond lengths (Å) and angles (deg): Cu–N43 1.951(3), Cu–N33 1.951(3), Cu–Cl1 2.2336(10), Cu–Cl2 2.2283(12), N(43)–Cu–N(33) 91.06(11), N(43)–Cu–Cl(2) 101.69(9), N(33)–Cu–Cl(2) 129.58(9), N(43)–Cu–Cl(1) 126.28(9), N(33)–Cu–Cl(1) 104.64(9), Cl(1)–Cu–Cl(2) 105.96(4).

Table 1. Copper-Catalyzed Homopolymerization of t-BA^a

catalyst	Cu/Al/ <i>t</i> -BA mole ratio	polymer yield (%)	$M_{ m n}, M_{ m w},$ MWD ($ imes 10^{-3}$)	tacticity mm, mr, rr (%)	
5	0/1/14	trace			
5	1/5/940	5			
5	1/12/1010	33	280, 620, 2.2	16, 45, 39	
5	1/13/1320	57	470, 850, 1.8		
5	1/12/980	77	320, 640, 2.0		
7b	1/10/980	52		19, 43, 38	
radical ^b				mm = 44 - 46	
radical ^c		99	54, 89, 1.66	mm = 44	
epimer-	1/12/1000	97	58, 92, 1.59	mm = 45	
ization ^d					

^{*a*} Reaction conditions: 0.045 mmol of catalyst; toluene as solvent; exclusion of light; mol Al/MAO; 25 °C; 18 h. ^{*b*} Reference 20. Polymers produced over a range of 0-60 °C. ^{*c*} Poly(*t*-BA) prepared with benzoyl peroxide as in ref 20. ^{*d*} Epimerization verification of polymer in footnote c. Mole ratio of *t*-BA based on monomer segments.

Activation of **5**–**7** with MAO generates active polymerization catalysts that homopolymerize both ethylene and acrylates, as well as copolymerize ethylene with acrylates. Under the copolymerization conditions described below, the order of monomer reactivity is *tert*-butyl acrylate (*t*-BA) 3910 (mol of monomer/(g of Cu h)) > *n*-butyl acrylate (*n*-BA) 1790 (mol of monomer/(g of Cu h)) > methyl methacrylate (MMA) 860 (mol of monomer/(g of Cu h)). CuBBIM/MAO does not homopolymerize traditional free radically polymerizable monomers such as styrene, vinyl acetate, or butadiene. Also, unlike Brookhart's Pd diimine catalysts, it does not homopolymerize cyclopentene.¹⁹

Homopolymers of ethylene prepared by CuBBIM/ MAO at 700–800 psig ethylene, 80 °C, and Al/Cu ratio of >200/1 are typically high molecular weight, very linear, highly crystalline, and very high melting polymers (T_m > 135 °C). The ¹³C NMR of HDPE prepared by CuBBIM/MAO contains no detectable branches. This is in contrast to the first-generation Brookhart Pd diimine catalysts that often produce polymers with 80– 150 branches/1000 carbons.²¹

Homopolymerization of acrylates by CuBBIM/MAO is typically run at lower temperatures (~25 °C) and ratios of Al/Cu (<50). Table 1 shows the homopolymerization of *t*-BA by these CuBBIM/MAO catalyst systems. Conversion increases with increasing MAO/Cu ratio and longer reaction times. Little or no polymer is formed in the absence of the CuBBIM catalysts. GC and ¹H NMR analysis of the polymerization mixture showed only monomer, polymer, and solvent. The resulting products are high molecular weight, narrow MWD polymers. The

 Table 2. Copper-Catalyzed Copolymerization of Ethylene

 and t-BA^a

Cu/Al/ <i>t</i> -BA mole ratio	polymer yield (g)	$M_{ m n},M_{ m w},\ { m MWD}\ (imes 10^{-3})$	triads EAE:EAA:AAA	branches/ 1000 C	mol % <i>t</i> -BA ^b
1/230/1740 1/130/1780 1/230/950	6.0 5.9 2.4	39, 85, 2.2 44, 89, 2.0	6:35:58 6:34:60 11:35:54	0 6 10	65 72 55

^{*a*} Reaction conditions: 0.045 mmol of **7b**; toluene as solvent; exclusion of light; mol Al/MAO; 80 °C; 720 psig of ethylene; concentration *t*-BA 1.9 M. ^{*b*} Mole fraction of the copolymer consisting of *t*-BA units.

tacticities of the CuBBIM/MAO-catalyzed polymers are considerably different than those found for a free radically prepared poly(*t*-BA).

Ethylene and *tert*-butyl acrylate have been copolymerized at 600–800 psig and 80 °C using CuBBIM/ MAO catalysts. In contrast to the Brookhart Pd and Ni diimine catalysts, high levels of acrylate incorporation are possible (45–100 mol %). High molecular weight, narrow MWD copolymers with low levels of branching can be made (Table 2). The products have been shown to be true copolymers by ¹³C NMR and GPC/UV. The ¹³C NMR spectra for the CuBBIM/MAO catalyzed E/*t*-BA copolymers can be compared with homopoly-(*t*-BA). The presence of EAE and EAA/AAE triads in the former is a clear indication of copolymer formation. Additional support for the presence of copolymers is a uniform distribution of UV activities across the MWD in the GPC/UV trace.

While the mechanism of CuBBIM/MAO polymerizations is not fully determined, the ethylene homopolymerization data are consistent with a single-site coordination/insertion mechanism based upon the high degree of linearity and narrow MWD in the product. Along with the ability to incorporate certain α -olefins, this mechanism is further supported by indirect mechanistic studies performed using fluorine-labeled copper cata-lysts.^{14,22} The acrylate homopolymerization and copolymerization cases may proceed by a different or additional mechanism. However, conventional free-radical or ATRP mechanisms are less likely. Conventional freeradical chemistry is unlikely because CuBBIM/MAO does not polymerize other traditional free-radical monomers (e.g., styrene, butadiene, vinyl acetate) and can induce polymerization in the presence of known freeradical inhibitors such as phenothiazine or MEHQ. (Commercial samples of acrylate monomers containing 10-100 ppm of inhibitor can be polymerized "as received" without removal of inhibitor.) In our lab 6b failed to induce ATRP with PhEtCl or reverse ATRP with AIBN. Tacticities for acrylate homopolymers catalyzed by CuBBIM/MAO do not match those expected for free-radical products.²⁰ Attempts to epimerize a radically produced homopolymer of t-BA under CuBBIM/ MAO polymerization conditions failed to alter the tacticity of the polymer. Additionally, room temperature experiments monitoring the CuBBIM/MAO catalysis of the homopolymerization of *t*-BA by EPR failed to detect the presence of any radical or Cu(II) signal.

In summary, CuBBIM/MAO is a highly versatile catalyst system that homopolymerizes ethylene and acrylates and, more significantly, induces ethylene/ acrylate copolymerization. This new system is remarkable in spanning homopolymerization space broadly, while still enabling copolymerization of these traditionally transition-metal-catalyzed incompatible monomer classes.

Supporting Information Available: Complete details of the synthesis of 1-7; further details of crystallographic, polymerization, epimerization, and EPR studies; and tables in CIF format containing 2, 3b, 5, 5·H₂O, 6b, and 7a·1,2dichlorobenzene. This material is avaiable free of charge via the Internet at http://pub.acs.org.

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MA034548C