Polymerization Catalysts

Arylzinc Complexes as New Initiator Systems for the Production of Isobutene Copolymers with High Isoprene Content^{**}

Shaun Garratt, Antonio Guerrero, David L. Hughes, and Manfred Bochmann*

The production of butyl rubber by the copolymerization of isobutene (IB) and isoprene (IP) is an important industrial process. Commercially, polymerization is initiated by protons generated by an AlCl₃/H₂O slurry in chloromethane at low temperatures (ca. -100 °C).^[1-3] Incorporation of IP is typically of the order of 1-2%. However, under such conditions isoprene acts as a powerful retardant,^[4] and both polymer molecular weight and polymer yield decrease sharply with increasing IP concentration in the monomer feed. Copolymers with increased isoprene incorporation, and hence increased unsaturation in the main chain, are desirable since they are more compatible and better at cross-linking with other unsaturated polymer materials.

A number of Lewis acids have been employed as initiators for IB/IP copolymerizations. Mixtures of alkyl aluminum halides with alkyl halides are very efficient, although gel formation is still evident at higher concentrations of IP, and there is significant chain branching, even at -70 °C. Other examples include BCl₃,^[1,5] chelating boranes,^[6] and a variety of transition-metal halides, for example, TiCl₄, VCl₄, and FeBr₃,^[7-9] Organometallic Lewis acids paired with extremely weakly coordinating anions, such as [AlCp₂Me]/B(C₆F₅)₃,^[10] [SiMe₃][B(C₆F₅)₄],^[11] [Cp*TiMe₃]/B(C₆F₅)₃ (Cp* = C₅Me₅),^[12] and [(Cp^R)₂ZrX₂]/[CPh₃][B(C₆F₅)₄] (X = Me, H) (Cp^R = C₅H₄SiMe₃)^[13-15] have also been found effective. However, to our knowledge there are no reports to date on the use of zinc compounds in IB homo- and co-polymerizations.

Zinc compounds have the advantage of being nontoxic and relatively cheap compared to metallocene/borate initiators. We now found that they also allow the synthesis of highmolecular-weight copolymers with low gel content. Whereas anhydrous $ZnCl_2$ in the presence of *t*BuCl or MeCOCl was inactive in both neat IB and CH_3Cl , $[Zn(C_6F_5)_2]$ -toluene (readily obtained from $ZnMe_2$ and $B(C_6F_5)_3$) is sufficiently soluble in CH_2Cl_2 , IB, and IB/MeCl mixtures and reacts with suitable alkyl halides by ionization and initiation of IB

 [*] Dr. S. Garratt, A. Guerrero, Dr. D. L. Hughes, Prof. M. Bochmann Wolfson Materials and Catalysis Centre School of Chemical Sciences and Pharmacy University of East Anglia Norwich NR4 7TJ (UK) Fax: (+44) 160-359-2044 E-mail: m.bochmann@uea.ac.uk

2166 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

DOI: 10.1002/anie.200353787

^[**] This work was supported by Bayer AG, Leverkusen, and Bayer Inc., Canada. Gel quota determinations were carried out by Bayer AG, Leverkusen. We thank Dr. M. Bohnenpoll and Dr. M. Drewitt for helpful discussions.

polymerization [Eq. (1)]. Representative results are shown in Table 1.

$$[\operatorname{Zn}(\operatorname{C}_6\operatorname{F}_5)_2] + \operatorname{RX} \rightleftharpoons \operatorname{R}^+[\operatorname{ZnX}(\operatorname{C}_6\operatorname{F}_5)_2]^- \tag{1}$$

Variable-temperature NMR spectroscopy confirmed the formation of carbocations in this system. For example, mixtures of cumyl chloride and $[Zn(C_6F_5)_2]$ -toluene in CD_2Cl_2 at -78 °C show the signals of the PhCMe₂⁺ cation as well as those of phenyltrimethylindane, the product of cationic cyclization (Scheme 1).^[16,17]

The formation of nonnucleophilic zincate anions in this system was demonstrated by the reaction of Ph₃CCl with $[Zn(C_6F_5)_2]$ ·toluene. Upon mixing, the typical orange color of CPh₃⁺ ions was observed, and cooling to -20 °C afforded an oily precipitate from which crystalline $[CPh_3][Zn(C_6F_5)_3]$ was isolated. The anion $[Zn(C_6F_5)_3]^-$ is reminiscent of the "non-coordinating" perfluoroarylborates known from metallocene catalysis^[19,20] and is to our knowledge the first example of a zinc-based anion with sufficiently low nucleophilicity that it can stabilize carbocations.^[21]

The compound was characterized by X-ray diffraction.^[22] Both the cation and the anion have propeller structures, and in the crystal they are stacked on top of each other, with almost parallel C₆H₅ and C₆F₅ aryl substituents (Figure 1). While donor–acceptor π -stacking of aryl rings having different electron densities might be invoked, reminiscent of the well-known C₆H₆·C₆F₆ phases,^[23] the solid-state structure of [CPh₃][Zn(C₆F₅)₃] is simply the most economical way of packing cations and anions with threefold symmetry axes.

In the absence of alkyl halide, $[Zn(C_6F_5)_2]$ -toluene in neat IB affords only low yields of high-molecular-weight poly-(isobutene) (ca. 1.0 g in 60 min). Addition of isoprene reduces the yield (Table 1, entry 1). Polymer formation in these cases is presumably due to the reaction of the zinc Lewis acid with adventitious traces of water. Premixing $[Zn(C_6F_5)_2]$ -toluene and MeCOCl in CH₂Cl₂ at -78 °C prior to injection was unsuccessful; however, the addition of first 0.15 mmol MeCOCl then 0.15 mmol $[Zn(C_6F_5)_2]$ -toluene to the monomer resulted in rapid polymerization (ca. 10 % conversion in 1 min). In the presence of IP yields were found to drop significantly. Thus, with 1.5 mL isoprene in the feed, only 4 g copolymer was produced after 30 min ([Zn] = [MeCOCI] =2 mM). Higher IP concentrations reduced the yields still further, such that with a mixture of 90 mL IB/10 mL IP only



Scheme 1. Formation of carbocations in mixtures of alkyl chorides and $[Zn(C_6F_5)_2]$ -toluene in CD_2Cl_2 at $-78\,^{\circ}C.$





Figure 1. Top: Crystal structure of $[CPh_3][Zn(C_6F_5)_3]$ (ellipsoids at 50% probability). Selected bond lengths [Å] and angles [°]: Zn-C(11) 2.030(6), Zn-C(21) 1.981(10), Zn-C(31) 2.056(11), C(21)-Zn-C(11) 120.7(5), C(11)-Zn-C(31) 118.5(5), C(21)-Zn-C(31) 120.7(2). Bottom: View showing the eclipsed stacking of C_6H_5 and C_6F_5 rings, parallel to the *a* axis.

Table 1: (Co-)polymerizations of isobutene initiated by $[Zn(C_6F_5)_2]$ ·toluene/tBuCl.^[a]

Run	Zn [mmol]	tBuCl [mmol]	IB [mL]	IP [mL]	t [min]	Yield [g]	$\bar{M}_{\rm w}/10^5$	$ar{M}_{w}/ar{M}_{n}$	IP incorp. [mol%]	Gel quota [wt.%]
1	0.2	-	100	1.5	60	0.6	12.23	2.2	1.4	[b]
2	0.2	0.2	100	-	5	4.1	12.89	1.7	-	[b]
3	0.2	0.2	100	1.5	30	5.0	7.94	1.6	1.5	[b]
4	0.2	0.2	97	3	30	4.5	9.06	2.2	2.7	1.5
5	0.3	0.3	95	5	30	3.8	8.88	2.4	4.2	[b]
6	0.3	0.3	93	7	30	4.0	7.82	2.6	6.4	3.8
7	0.3	0.3	90	10	60	3.2	5.92	2.5	9.0	4.6
8	0.3	0.3	90	10	30	2.5	4.87	2.2	10.7	[b]
9	0.3	0.3	85	15	30	1.8	2.55	2.0	14.7	[b]

[a] Reaction conditions: $IB + IP \approx 100 \text{ mL}$, $-78 \,^{\circ}$ C. Polymerizations terminated by the injection of methanol. [b] Not determined.

Angew. Chem. Int. Ed. 2004, 43, 2166-2169

www.angewandte.org

Communications

ca. 0.5 g copolymer was obtained after 30 min. The polymer molecular weights were also lower than we had hoped.

Much higher conversions and polymer molecular weights resulted when tert-butyl chloride was used as a coinitiator with $[Zn(C_6F_5)_2]$ -toluene (Table 1).^[24] Most reactions were conducted in neat monomer (ca. 100 mL total volume, [Zn] =[tBuCl] = 2 mM) at $-78 \,^{\circ}\text{C}$, with the zinc component being added last. High reactivity was observed (e.g. 4.1 g polymer after 5 min), and polymers of high molecular weights ($\bar{M}_{\rm w} \approx$ 1.3×10^6) and low polydispersities $(\bar{M}_w/\bar{M}_n \approx 1.7-2)$ were obtained. Addition of isoprene resulted in a general decrease in activity and polymer molecular weights but much less so than with the MeCOCl system described above. Thus, with IB/IP = 100:1.5 (mL), 5 g of copolymer was obtained after 30 min, with a high $\bar{M}_{\rm w}$ of $8 \times 10^5 \, {\rm g\,mol^{-1}}$ and $\bar{M}_{\rm w}/\bar{M}_{\rm n} = 1.6$ (Table 1, run 3). Under these conditions when $[Al(C_6F_5)_3]$ was used in place of $[Zn(C_6F_5)_2]$, a poorly soluble, extensively cross-linked polymer resulted. Increasing the isoprene con-

centration still further led to a

slow drop-off in activity, although the molecular weights remained high, with $\bar{M}_{\rm w} \approx 5 \times 10^5 \, {\rm g \, mol^{-1}}$ at ca. 10 mol% IP incorporation and

14.7 mol% IP (Table 1, runs 8 and 9). While some initiator systems give an increase in molecular weight at high IP feed as the result of increased branching and cross-linking, there is remarkably little evidence for this here (Figure 2). Incorporation of isoprene was found to increase linearly with the feed concentration.

As evident in Figure 3 and

Table 2, the molecular weight decreases with increasing polymer-

at

ca.

 $\bar{M}_{\rm w} \approx 2.5 \times 10^5 \,\mathrm{g \, mol^{-1}}$



Figure 3. Trends in M_w of IB/IP copolymers (1.5 vol% IP feed) as a function of temperature for the $[Zn(C_6F_5)_2]/tBuCl (\bullet)$ and $[Et_2AlCl]/tBuCl$ (**•**) systems, respectively. [Zn] = [tBuCl] = 2 mm; [Al] = 16 mm, $[tBuCl] = 1.15 \times 10^{-3} \text{ mm}$.

Table 2: Temperature dependence of IB polymerizations initiated by $[Zn(C_6F_5)_2]$ ·toluene/tBuCl.

Run	Zn [mmol]	tBuCl [mmol]	IB [mL]	IP [mL]	т [°С]	t [min]	Yield [g]	$\bar{M}_{\rm w}/10^5$	$ar{M}_{ m w}/ar{M}_{ m n}$	IP incorp. [mol%]
1	0.2	0.2	100	1.5	-78	30	5.0	7.94	1.6	1.5
2	0.1	0.1	100	1.5	-50	10	3.9	4.36	1.8	1.4
3	0.1	0.1	100	1.5	-35	10	5.6	3.10	1.7	1.5

Table 3: Poly	merizations with	$[Zn(C_6F_5)_2]$	/tBuX	(X = Br, I)	[a]
---------------	------------------	------------------	-------	-------------	-----

Run	Х	Zn [mmol]	[tBuX] [mmol]	IB [mL]	IP [mL]	Yield [g]	$\bar{M}_{ m w}/10^5$	$ar{M}_{ m w}/ar{M}_{ m n}$	IP incorp. [mol%]
1	Br	0.3	0.6	95	5	3.9	4.12	2.3	5.2
2	Br	0.1	0.5	95	5	2.0	8.75	2.3	5.1
3	I	0.3	0.6	95	5	2.7	4.26	2.0	5.5

[a] Reaction conditions: -78 °C, 30 min; initiator stock solutions in CH₂Cl₂ at -78 °C; polymerizations terminated by the injection of methanol.



Figure 2. Plot of \overline{M}_{w} in IB/IP copolymers versus the degree of IP incorporation (*n*(IP)). Polymerization temperature = -78 °C.

ization temperature, as expected. At all temperatures the \bar{M}_w values obtained with the zinc system are substantially higher than those of polymers made with a classical [Et₂AlCl]/*t*BuCl initiator^[3b] under comparable conditions.

The activity of the new initiator system can be improved by increasing the *t*BuCl/Zn ratio, or by using *t*BuBr or *t*BuI as the halide source (Table 3). With *t*BuBr there was some improvement in polymerization rate. For example, with [Zn] = 3 mM, >10% conversion was obtained after 1 min, which made it necessary to decrease the zinc concentration to control the reaction. This, in turn, led to increased polymer molecular weights.

In summary, the Lewis acidic zinc complex $Zn(C_6F_5)_2$ in combination with *t*BuX provides the first highly efficient initiator system for isobutene/isoprene copolymerizations based on zinc. Up to 14.7 mol% isoprene incorporation has been realized, without significant cross-linking or gelation. We are currently exploring the scope of this new system.

Received: January 19, 2004 [Z53787] Published Online: March 15, 2004

2168 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.angewandte.org



Keywords: anions \cdot copolymerization \cdot isobutene \cdot Lewis acids \cdot zinc

- a) J. P. Kennedy, E. Maréchal, Carbocationic Polymerization, Wiley, New York, **1982**; b) J. P. Kennedy, B. Iván, Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice, Hanser, Munich, **1991**; c) P. H. Plesch, Macromol. Symp. **1994**, 85, 1.
- [2] O. Nuyken, S. D. Pask in *Comprehensive Polymer Science*, Vol. 3 (Eds.: G. Allen, J. C. Bevington), Pergamon, Oxford, **1989**, p. 619.
- [3] a) J. P. Kennedy, Polymer Chemistry of Synthetic Elastomers, Interscience, New York, **1968**, chap. 5; b) J. P. Kennedy, P. D. Trivedi, Adv. Polymer Sci., **1978**, 28, 83; c) J. P. Kennedy, P. D. Trivedi, Adv. Polym. Sci. **1978**, 28, 115.
- [4] a) H. Güterbock, Polyisobutylen und Isobutylen-Mischpolymerisate, Springer, Berlin, 1959; b) J. P. Kennedy, R. G. Squires, Polymer 1965, 6, 579.
- [5] B(Al)Cl₃: a) E. Marechal, L. Bull, H. A. Nguyen, *Polym. Bull.* **1987**, *17*, 157; b) L. Balogh, L. Wang, R. Faust, *Macromolecules* **1994**, *27*, 3453; c) L. Balogh, Z. Fodor, T. Kelen, R. Faust, *Macromolecules* **1994**, *27*, 4648; d) J. P. Kennedy, S. C. Feinberg, S. Y. Huang, *J. Polym. Sci. Polym. Chem. Ed.* **1978**, *16*, 243; e) D. W. Grattan, P. H. Plesch, *Makromol. Chem.* **1980**, *181*, 751; f) R. F. Storey, T. L. Maggio, *Macromolecules* **2000**, *33*, 681; g) M. Bahadur, T. D. Shaffer, J. R. Ashbaugh, *Macromolecules* **2000**, *33*, 9548.
- [6] S. P. Lewis, N. J. Taylor, W. E. Piers, S. Collins, J. Am. Chem. Soc. 2003, 125, 14686.
- [7] VCl₄: a) M. Marek, L. Toman, J. Polym. Sci. Polym. Symp. 1973, 42, 339; b) L. Toman, M. Marek, J. Jokl, J. Polym. Sci. Part A 1974, 12, 1897; c) L. Toman, M. Marek, Polymer 1981, 22, 1243; d) L. Toman, M. Marek, J. Macromol. Sci. Chem. 1981, 15, 1533.
- [8] FeX₃: a) M. Marek, J. Pecka, V. Halaška, *Makromol. Chem. Macromol. Symp.* **1988**, *13–14*, 443; b) M. Marek, J. Pecka, V. Halaška, *Macromol. Chem. Phys.* **1995**, *196*, 2709.
- [9] TiCl₄: a) L. Toman, J. Pilař, M. Marek, *J. Polym. Sci. Part A* 1978, *16*, 371; b) I. Majoros, T. M. Marsalkó, J. P. Kennedy, *J. Polym. Sci. Part A* 1996, *34*, 1675; c) A. Nagy, I. Majoros, J. P. Kennedy, *J. Polym. Sci. Part A* 1997, *35*, 3341; d) X. Cao, R. Faust, *Macromolecules* 1999, *32*, 5487; e) H. Schlaad, Y. Kwon, L. Sipos, R. Faust, B. Charleux, *Macromolecules* 2000, *33*, 8225; f) R. F. Storey, A. B. Donnalley, *Macromolecules* 2000, *33*, 53; g) R. F. Storey, C. L. Curry, L. K. Hendry, *Macromolecules* 2001, *34*, 5416; h) L. Sipos, X. Y. Cao, R. Faust, *Macromolecules* 2001, *34*, 456; i) H. Mayr, H. Schimmel, S. Kobayashi, M. Kotami, T. R. Prabakaran, L. Sipos, R. Faust, *Macromolecules* 2002, *35*, 4611; j) R. M. Peetz, A. F. Moustafa, J. P. Kennedy, *J. Polym. Sci. Part A* 2003, *41*, 740.
- [10] M. Bochmann, D. M. Dawson, Angew. Chem. 1996, 108, 2371; Angew. Chem. Int. Ed. Engl. 1996, 35, 2226.
- [11] S. Jacob, Z. J. Pi, J. P. Kennedy, Polym. Bull. 1998, 41, 503.
- [12] a) M. C. Baird, *Chem. Rev.* 2000, 100, 1471; b) M. Lin, M. C. Baird, *J. Organomet. Chem.* 2001, 619, 62; c) K. R. Kumar, C. Hall, A. Penciu, M. J. Drewitt, P. J. McInenly, M. C. Baird, *J. Polym. Sci. Part A* 2002, 40, 3302.
- [13] a) A. G. Carr, D. M. Dawson, M. Bochmann, *Macromolecules* 1998, 31, 2035; b) X. Song, M. Thornton-Pett, M. Bochmann, *Organometallics* 1998, 17, 1004; c) A. G. Carr, D. M. Dawson, M. Bochmann, *Macromol. Rapid Commun.* 1998, 19, 205.
- [14] a) T. D. Shaffer, J. R. Ashborough, *J. Polym. Sci. Part A* 1997, *35*, 329; b) M. Vierle, Y. Zhang, E. Herdtweck, M. Bohnenpoll, O. Nuyken, F. E. Kühn, *Angew. Chem.* 2003, *115*, 1345; *Angew. Chem. Int. Ed.* 2003, *42*, 1307.
- [15] S. Garratt, A. G. Carr, G. Langstein, M. Bochmann, *Macro-molecules* 2003, 36, 4276.

Angew. Chem. Int. Ed. 2004, 43, 2166-2169

www.angewandte.org

- [17] F. Ciminale, L. Lopez, V. Paradiso, A. Nacci, *Tetrahedron* 1996, 52, 13971.
- [18] Above $-80 \,^{\circ}$ C in the absence of monomer, deprotonation of the cumyl cation and hydrolysis of $[Zn(C_6F_5)_2]$ to $ZnCl_2$ and C_6F_5H is also observed.

[16] D. A. Walker, T. J. Woodman, D. L. Hughes, M. Bochmann,

Organometallics 2001, 20, 3772

- [19] a) E. Y. X. Chen, T. J. Marks, *Chem. Rev.* 2000, 100, 1391; b) M. Bochmann, J. Chem. Soc. Dalton Trans., 1996, 255; c) M. Bochmann, Angew. Chem. 1992, 104, 1206; Angew. Chem. Int. Ed. Engl. 1992, 31, 1181.
- [20] a) A. J. Lupinetti, S. H. Strauss, Chemtracts: Inorg. Chem. 1998, 11, 565; b) S. H. Strauss, Chem. Rev. 1993, 93, 927.
- [21] For Li and Mg salts of triarylzincates see for example: K. Thiele, H. Görls, W. Seidel, Z. Anorg. Allg. Chem. 1998, 624, 555; M. Krieger, G. Geiseler, K. Harms, J. Merle, W. Massa, K. Dehnicke, Z. Anorg. Allg. Chem. 1998, 624, 1387.
- [22] Crystal data: $C_{37}H_{15}F_{15}Zn$, $M_w = 809.9$, monoclinic, space group C2/c (no. 15), a = 8.219(11), b = 20.905(6), c = 18.367(8) Å, $\beta =$ 95.51(6)°, V = 3141(5) Å³, Z = 4, $\rho_{calcd} = 1.713$ g cm⁻³; F(000) = 1608, T = 140(1) K, $\mu(Mo_{K\alpha}) = 9.0$ cm⁻¹, $\lambda(Mo_{K\alpha}) = 0.71069$ Å. A crystal of dimensions $0.8 \times 0.40 \times 0.20$ mm was mounted in oil on a glass fiber and fixed in the cold nitrogen stream on a Rigaku/ \dot{MSC} AFC7R diffractometer equipped with $Mo_{K\alpha}$ radiation and graphite monochromator. 3607 reflections to $\theta_{max} = 25^{\circ}$, of which 2773 were unique ($R_{int} = 0.060$) and 2282 "observed" ($I > 2\sigma_I$); $wR_2 = 0.163$ and $R_1 = 0.066$ (2B) for all 2773 reflections; w = $[\sigma^2(F_o^2) + (0.108P)^2 + 2.35P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; $R_1 = 0.059$ for "observed" reflections. CCDC 228529 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
- [23] a) C. R. Patrick, G. S. Prosser, *Nature* **1960**, *187*, 1021; b) J. H. Williams, J. K. Cockcroft, A. N. Fitch, *Angew. Chem.* **1992**, *104*, 1666; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1655; c) J. H. Williams, *Acc. Chem. Res.* **1993**, *26*, 593.
- [24] Polymerizations were carried out in a flame-dried all-glass 250mL three-necked vessel following the procedures detailed in ref. [15]. Stock solutions of $[Zn(C_6F_5)_2]$ -toluene and *t*BuX were prepared separately in cold $(-78 \,^\circ\text{C}) \text{ CH}_2\text{Cl}_2$, $[Zn] = 0.1 \,^{\text{M}}$ and $[tBuX] = 0.01-0.1 \,^{\text{M}}$ (X = Cl, Br or I). Polymers were analyzed by size-exclusion chromatography in THF at 25 $\,^\circ\text{C}$ using a Polymer Laboratories GPC-220 instrument equipped with a dual refractive index/light-scattering detector.