"Highly Reactive" Poly(isobutene)s via Room Temperature Polymerization with a New Zinc-Based Initiator System

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Polyisobutenes (PIBs) are important materials in the chemical industry that find different applications depending on their molecular weights.[1] Thus, high molecular weight polymers (M_n > 100 000 g mol^{-1}) are mainly used as inner liners in the manufacture of tires due to their damping properties and low gas permeability, while low to medium molecular weight PIBs (M_n = 5000−100 000 g mol^{-1}) are commonly used in sealants and adhesives. Low molecular weight polymers containing more than 60% terminal double bonds are of special interest as intermediates in the preparation of additives to lubricants (M_n = 2000−40 000 g mol^{-1}) and fuels (M_n = 150−5000 g mol^{-1}).[2] These polyisobutenes can be chemically modified by epoxidation or reaction with maleic anhydride.[2,3] A high content of vinylidene end groups is desired since only terminal double bonds react at a sufficiently high rate; these materials are therefore referred to as "highly reactive" PIBs. Industrially these materials are prepared by a carbocationic mechanism at low temperatures, using Lewis acid initiators such as aluminum chloride or boron trifluoride.[4−6] Medium to low molecular weight polyisobutenes with more than 80% terminal double bonds have only been produced in good yields at temperatures well below 0 °C.[6,7] Only recently, an interesting system has been reported, based on $[Mn(NCMe)_6]^{2+}$ salts of noncoordinating borate anions such as $[C_3H_3N_2\{B(C_6F_5)_3\}_2]^-$, that operates at higher temperatures (+20 to +60 °C) to produce terminally unsaturated PIBs.[8] However, this system failed to provide medium molecular weight polymers and required unusually long polymerization times, e.g., 16 h to reach up to 88% conversion in isobutene (IB) homopolymerizations.[8b]

We recently reported the first zinc-based initiator system for IB polymerizations, $Zn(C_6F_5)_2$·toluene/RCl (R = *t*Bu, $PhCMe_2$), which is highly effective for the synthesis of high-MW isoprene-rich PIB.[9] The search for cheaper initiator systems that do not rely on transition metal components, elaborate noncoordinating anions, or expensive C_6F_5 derivatives has led us to explore simpler zinc halide systems. We report here a new type of polymerization initiator based on the reaction of alkylzinc chloride with alkyl halides which gives medium molecular weight PIBs containing up to 92% vinylidene end groups. To our knowledge this is the first system to provide such polymers at room temperature in fast reaction times (ca. 30 min).

The addition of EtZnCl, prepared by comproportionation of $ZnCl_2$ and $ZnEt_2$[10] and used either as a solid or as a CH_2Cl_2 slurry, to a solution of IB in CH_2Cl_2 (v/v 1:2) containing *t*BuCl at room temperature led to rapid polymerization (Table 1). In contrast to our previous work with soluble initiators where optimum results were obtained in neat IB,[11,15b] this system works best in chlorocarbons at ambient temperatures to give medium molecular weight PIBs. By contrast, reactions under the same conditions in toluene did not give polymers.

The method of introducing the zinc component into the mixture is crucial for the success of the polymerization. Thus, premixing EtZnCl and *t*BuCl in CH_2Cl_2 either at low temperature or at 20 °C immediately gave a white precipitate (bulk $ZnCl_2$) which when injected into IB/CH_2Cl_2/*t*BuCl mixtures produced only traces of polymer. There is no polymerization with EtZnCl in the absence of *t*BuCl. The effectiveness of zinc compounds to act as polymerization initiators depends on both their Lewis acidity and their solubility; for example, mixtures of $ZnEt_2$ and *t*BuCl in CH_2Cl_2 proved inactive, as was powdered $ZnCl_2$ due to its insolubility.

The reaction of EtZnCl and *t*BuCl in CD_2Cl_2 was monitored by ^{1}H NMR spectroscopy from −30 to 20 °C. The presence of carbocationic species could not be confirmed under these conditions due to the high reactivity of the *tert*-butyl cation; however, the rapid formation of $ZnCl_2$ and isobutene oligomers was observed. The analogous reaction of EtZnCl with trityl chloride rapidly gave an orange solution, and a significant amount of solid was formed ($ZnCl_2$). High-intensity signals for the trityl cation were unambiguously identified at −30 °C (δ 7.73, 7.94, and 8.31). The CPh_3^+ signals broadened on warming to +5 °C and disappeared at 20 °C. Formation of a complex mixture of ethylene, triphenylmethane, 1,1,1-triphenylpropane, trityl cation, and the unreacted starting material was observed at −10 °C; the assignment of these species was validated by comparison with the chemical shifts of authentic samples.[12] These products are consistent with the decomposition of a trityl zincate intermediate, $[CPh_3][ZnCl_2Et]^-$, via competing β-hydride abstraction and ethyl abstraction pathways (Scheme 1). It is therefore possible that the mode of initiation by EtZnCl/*t*BuCl involves not only $[CMe_3]^+[ZnCl_2Et]^-$ but also the in-situ formation of molecular $ZnCl_2$. Although not conclusively proven, it seems likely that the latter is sufficiently reactive to abstract chloride from excess *t*BuCl to give $[CMe_3]^+[ZnCl_3]^-$.

The reactions in Table 1 were carried out by addition of EtZnCl into IB/CH_2Cl_2/*t*BuCl mixtures at 20 °C. EtZnCl was used in excess to act as a scavenger and as co-initiator, and *t*BuCl was employed as the limiting reagent. High concentrations of *t*BuCl (entries 6 and 7) gave rise to nearly quantitative conversions after 30 min reaction time. Molecular weight distributions were in the range $\bar{M}_w/\bar{M}_n$ = 1.9−2.5 and showed monomodal behavior. The polymers were of medium molecular weights, $\bar{M}_n$ = 10 000−29 000 g mol^{-1}.

Molecular weights gradually increased with decreasing *t*BuCl concentration up to ca. 5 mM (entry 5). With a further decrease of the initiator concentration a steep increase in the molecular weight was observed to give up to ca. $\bar{M}_n$ = 27 000 g mol^{-1} (entry 1). Conversion increased with [*t*BuCl] up to a 95%. A further increase in [*t*BuCl] raised the conversion slightly but decreased the molecular weight (entries 6 and 7).

Vierle et al. have previously analyzed the terminal to internal double bond ratios of polyisobutene samples by ^{1}H NMR analysis of the terminal end groups.[8b] Figure 1 shows a typical ^{1}H NMR spectrum of a PIB obtained with EtZnCl/*t*BuCl at room temperature. The expansion of the olefinic region (inset) shows

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Table 1. Isobutene Homopolymerizations at 20 °C[a]

entry	EtZnCl [10^{-3} mol/L]	*t*BuCl [10^{-3} mol/L]	yield [g]	conv [%]	initiator efficiency[b]	$\bar{M}_n \times 10^{-3}$ [g/mol][c]	PDI[c]	terminal C=C content [%][d]
1	2.1	1.6	0.42	6.8	0.31	26.9	1.9	92
2	3.3	2.5	0.82	13.2	0.42	24.9	1.9	90
3	3.9	2.9	0.97	15.6	0.37	28.9	1.6	87
4	4.3	3.2	1.35	21.7	0.48	28.1	1.6	85
5	6.4	4.8	1.90	30.6	0.74	16.9	2.0	85
6	19.3	14.5	5.9	95.0	0.90	14.5	2.0	60
7	38.7	29.0	5.9	98.0	0.65	10.1	2.5	60

[a] Conditions: solvent CH_2Cl_2, $V_{total} = 31$ mL, $[IB]_0 = 3.57$ M, reaction time 30 min, $T = 20$ °C. [b] Initiator efficiency based on limiting [*t*BuCl]. [c] Determined by gel permeation chromatography calibrated with polystyrene standards. [d] Determined by ^{1}H NMR spectroscopy.

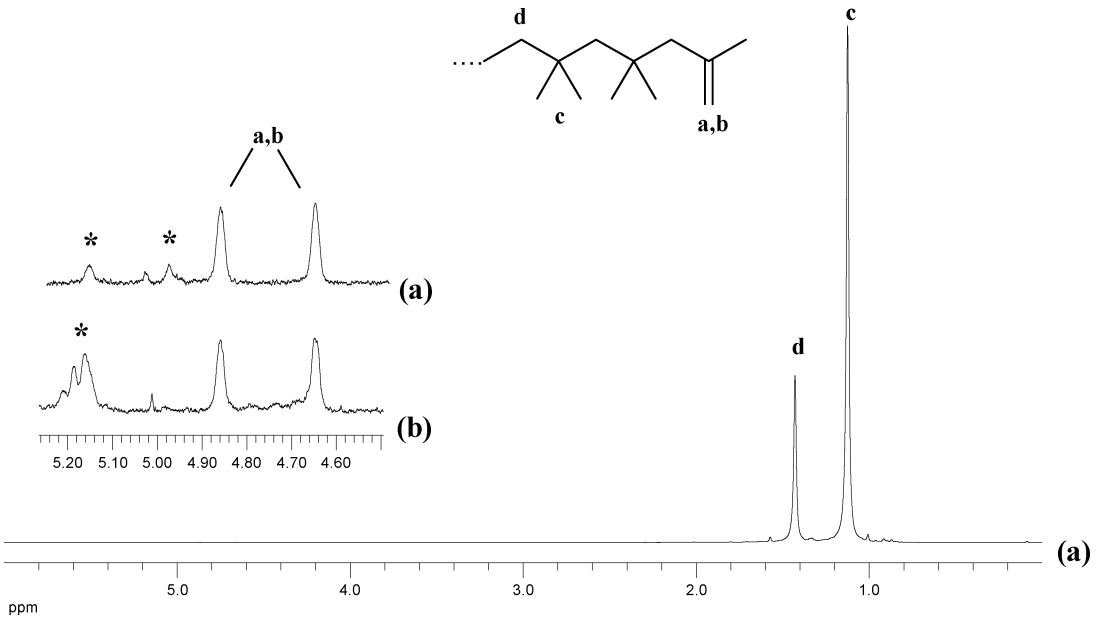
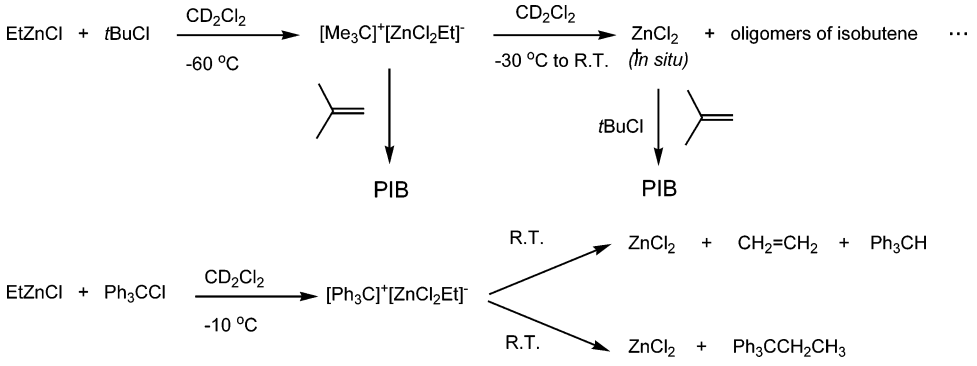


Figure 1. ^{1}H NMR assignment for homopolyisobutene samples containing high ratios of terminal double bonds. Inset: (a) [IB]/[Zn] = 2200, (b) [IB]/[Zn] = 120.

Scheme 1. Reactions of EtZnCl with Alkyl Halides



two signals at $\delta = 4.65$ and 4.86 for the terminal vinylidene end groups. Spectrum (a) corresponds to the polymer obtained in Table 1, entry 1, a polymerization carried out with a large monomer-to-initiator molar ratio (ca. 2200:1). Under these conditions, polymers contain up to 90% terminal olefinic end groups, the remaining 10% being internal olefins (marked with an asterisk). Expansion (b) is taken from a homopolymer sample (run 7) obtained at [monomer]:[initiator] = 120:1. In this case, the proportion of terminal olefinic end groups was ca. 60%. This makes these polymers interesting as potential intermediates, for example, as oil or lubricants additives.

Isobutene is frequently copolymerized with isoprene (IP) to give copolymers suitable for a subsequent bromination/dehydrobromination sequence to give products with reactive terminal double bonds for improved curing properties.[13] The EtZnCl/*t*BuCl system was therefore tested in IB/IP copolymerizations. Conditions were chosen so as to avoid exotherms and to ensure complete temperature control (ca. 20% conversion). IP incorporations of up to ca. 4 mol % were obtained with no significant decrease of the polymer yield (Table 2). The molecular weights of the copolymers were remarkably similar to those for IB homopolymers and decrease only slightly with increasing IP content. The polydispersities were monomodal and increased moderately with increasing IP incorporation but remained in the range 1.7−2.2.

The ^{1}H NMR spectra of the copolymers show that isoprene is incorporated in 1,4-trans fashion (see Supporting Information). By comparison with previous reports,[14] the intensity of the branching point at δ 4.93 is considerably higher: for every six isoprene units incorporated into the polymer chain, one generates

Table 2. IB/IP Copolymerizations with EtZnCl/*t*BuCl at 20 °C[a]

run	IP [mL]	yield [g]	IP-incorp [mol %]	$\bar{M}_n \times 10^{-3}$ [g/mol]	$\bar{M}_w \times 10^{-3}$ [g/mol]	PDI
8	0.2	1.26	0.6	22.9	40.3	1.7
9	0.3	1.35	1.2	21.0	37.5	1.8
10	0.4	1.34	2.1	18.7	34.6	1.8
11	0.5	1.10	2.7	16.0	31.2	1.9
12	0.7	0.94	3.4	14.3	31.7	2.2
13	0.8	0.98	3.9	16.1	32.3	2.0

[a] Conditions: solvent CH_2Cl_2, $V_{total} = 31$ mL, $[IB]_0$ 3.57 M; [EtZnCl] = [*t*BuCl] = 9.6 mM, $T = 20$ °C, time = 30 min.

a branching point. The mechanism of formation of this branching point is thought to go through a 1,4-addition followed by rearrangement and subsequent IB addition, as suggested by White et al.[14]

In conclusion, EtZnCl in combination with *t*BuCl provides a highly efficient system for the synthesis of vinylidene-terminated medium molecular weight polyisobutenes at room temperature. These "highly reactive" PIBs contain from 60% to 92% terminal double bonds. The system is equally effective in IB/IP copolymerizations with no significant decrease in reaction rates, polymer yields, or molecular weights. We are currently exploring the scope of this system.

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

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