In Situ Quenching Methods Toward *exo*-Olefin-Terminated Polyisobutylene

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Summary: *exo*-Olefin-terminated polyisobutylene was obtained directly from living isobutylene polymerizations by addition of a quenching compound to the living chain ends. Three broad classes of compounds were evaluated including hindered bases such as hindered pyridines and piperidines, *N*-hydro-2,5-disubstitutedpyrroles, and sulfides, ethers, and silylethers. The proposed mechanism of quenching unique to each class was discussed, with supporting kinetic, spectroscopic, and structure-based evidence presented. Hindered bases were proposed to operate by E2 elimination reaction of free base at the carbenium ion. *N*-Hydro-2,5-disubstitutedpyrroles were proposed to form the η^5-2,5-disubstitutedpyrrolyltrichloro-titanium(IV) coordination complex, which serves as the true quencher. Sulfides, ethers, and silylethers were proposed to operate by first converting the PIB chain ends quantitatively to the onium adduct, which is then decomposed to form *exo*-olefin PIB. Sulfides and ethers were the best performing quenchers of all the types studied, particularly bulky ones such di-*tert*-butylsulfide and diisopropyl ether.

Keywords: end-quenching; *exo*-olefin; living carbocationic polymerization; polyisobutylene

Introduction

Polyisobutylene (PIB) is a fully saturated hydrocarbon polymer with large-scale commercial applications as a gas-impermeable synthetic rubber and as the basis for lubricating oil and fuel additives. Low molecular weight olefin-terminated polyisobutylene (PIB) is of great commercial and scientific interest, and many important end group functionalization reactions proceed through the intermediacy of a terminal double bond.[1,2] For example, *exo*-olefin (i.e., isobutenyl or methyl vinylidene)-terminated PIB is a key intermediate toward hydroxyl,[3] phenol,[4] epoxide,[5] and sulfonic acid [6]-terminated PIB. PIB-succinic anhydride (PIBSA),[7] a notable commercial intermediate critical toward the synthesis of dispersants for lubricating oils, is formed by the thermal ene reaction of maleic anhydride with low molecular weight *exo*-olefin-terminated PIB.[8,9] Commercial olefin-terminated PIBs are formed using either the so-called "conventional" process based on a mixed C4 monomer stream and $AlCl_3$ (or $EtAlCl_2$) catalyst or the BF_3/alcohol–catalyzed process, which uses pure isobutylene monomer and yields so-called highly reactive PIB with a higher content of *exo*-olefin end groups (70–90% of the chains[10]). Recently, several groups have reported experimental catalyst systems consisting of $AlCl_3$/ether or $FeCl_3$/ether complexes,[11–15] which also produce highly reactive PIB with a high *exo*-olefin content. In general, all of these processes are chain transfer-dominated polymerizations or involve protic initiation and therefore cannot be used to produce difunctional (*telechelic*) olefin-terminated PIB.

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A number of methods have been reported, which enable the synthesis of both monofunctional and difunctional PIBs with near-quantitative *exo*-olefin functionality. Kennedy *et al.* introduced a method that was to become the standard route to di- and polyfunctional *exo*-olefin-terminated PIB for many years.[16] Theirs was a two-step method, wherein *tert*-chloride-terminated PIB was first synthesized via the inifer method,[17] and then regiospecific dehydrochlorination of the chain ends was carried out by reaction with potassium *tert*-butoxide in refluxing THF for 20–24 h. However, it was later shown that this process does not produce exclusively *exo*-olefin chain ends, but also leads to 5–8% *endo* olefin.[18]

Kennedy and coworkers[19,20] also reported the first *in situ* synthesis of olefin-terminated PIB, by addition of allyltrimethylsilane to a quasiliving carbocationic polymerization of isobutylene (IB). In 1997, Iván *et al.* showed that difunctional *exo*-olefin PIB could be made in an analogous process using methallyltrimethylsilane.[21]

In 2005, Storey and coworkers reported an *in situ* quenching method yielding quantitative *exo*-olefin PIB through controlled elimination rather than addition. They showed that quasiliving PIB may be reacted with certain hindered bases, such as 2,5-dimethylpyrrole (25DMP) and 1,2,2,6,6-pentamethylpiperidine (PMP), to produce *exo*-olefin termini directly from the polymerization reaction.[22] The principle limitation of the method was reported to be formation of coupled PIB at high chain end concentrations. Subsequently, Storey and Kemp showed that similar results could be obtained by quenching quasiliving PIB with an alkoxysilane or dialkyl ether.[23]

Recently, Storey *et al.* reported that organic sulfides were effective *in situ* quenchers for the production of *exo*-olefin PIB.[24,25] They showed that when a dialkyl or diaryl sulfide is added to a $TiCl_4$-catalyzed quasiliving polymerization of isobutylene, it immediately forms a complex with $TiCl_4$, and this complex reacts with the carbenium ions as they are formed (monomer consumption ceases), to yield the corresponding sulfonium ion. The sulfonium ions thus obtained were shown to be stable at low temperatures ($T \leq 20°C$), and their structures were characterized by NMR spectroscopy. Subsequent addition of a base, such as an amine or alcohol, followed by Lewis acid decomposition with methanol, was shown to decompose the sulfonium ion to form predominantly *exo*-olefin.

In this paper, for each of the various quencher types discussed above, we discuss the mechanism of quenching and the reaction conditions that maximize the yield of *exo*-olefin PIB, particularly under conditions of high chain end concentration [CE], which tend to promote coupling. We also compare the various methods with regard to ease of execution and how closely the product approaches the ideal of 100% *exo*-olefin end groups.

Experimental Part

Procedures for the synthesis and end-group analysis of *exo*-olefin PIB have been published.[22,23,25] Specific reactions conditions can be found in the figure captions and tables. In general, polymerization and quenching were performed within a N_2-atmosphere glove box equipped with a cryostated heptane bath and an infrared probe for monitoring IB conversion. Reactions were carried out in 60/40 (v/v) hexane/methyl chloride (Hex/MeCl) solvent mixtures at -60°C. The polymerization initiator was 2-chloro-2,4,4-trimethylpentane (TMPCl). 2,6-Lutidine (26Lut) was used as a proton trap and common ion salt precursor during IB polymerization, and it also served as proton acceptor for 25DMP quenching. The total [$TiCl_4$] indicated in the figure captions and tables was often added in two increments: one at the point of initiation of polymerization and the other after addition of the quencher.

The quencher was added at complete IB conversion and allowed to react for 30 min

Table 1.
Effect of Sulfide Structure on Polyisobutylene End-Group Composition.

Entry	Sulfide	Term. temp.[a] (°C)	PIB End-Group Composition (mol %) using ^{1}H NMR				
			exo-olefin	*endo*-olefin	Coupled	^{t}Cl	ether
1	di-*tert*-butyl sulfide	−20	100.0	0.0	0.0	0.0	0.0
		−40	100.0	0.0	0.0	0.0	0.0
		−60	100.0	0.0	0.0	0.0	0.0
2	diisopropyl sulfide	−20	98.0	02.0	0.0	00.0	00.0
		−40	90.5	01.8	1.8	02.3	03.6
		−60	75.3	03.8	1.5	06.4	13.0
3	dimethyl sulfide	−20	55.0	13.2	1.6	12.6	17.6
		−40	51.5	11.8	1.0	16.2	19.4
		−60	50.6	11.1	1.5	11.7	19.0
4	di-*n*-butyl sulfide	−20	39.0	9.3	4.0	40.0	07.7
		−40	37.5	6.7	3.0	44.5	08.3
		−60	36.0	5.7	2.1	44.3	11.9

Hex/MeCl = 60/40 (v/v); IB = 1.5 M; [CE] ≅ [TMPCl] = 0.039 M; [26Lut] = 0.005M; [sulfide]/[CE] = $[TiCl_4]$/[CE] = 4.0; [TEA]/[CE] = 1.2.
[a] Polymerization and quenching temperature = −60°C; reaction was slowly warmed and aliquots were terminated with excess methanol at the indicated temperature.

prior catalyst destruction using excess methanol. The only exception was sulfide quenching when used with optional proton acceptor triethylamine (TEA) (Tables 1 and 2). In this case, after the sulfide had been allowed to react for 30 min at −60 °C, TEA was added and reaction was allowed to proceed for an additional 30 min at −60 °C. Then an aliquot of the reaction was removed and terminated with excess pre-chilled methanol at −60 °C. The balance of the reaction was allowed to slowly warm (about 0.33 °C/min), and additional aliquots were optionally withdrawn at various termperatures, e.g. −40 °C, and terminated with excess pre-chilled methanol. Finally, the remaining reaction mixture was terminated at −20 °C by addition of excess pre-chilled methanol.

Results and Discussion

Hindered Base Quenchers

The effectiveness of certain basic, nitrogen-containing quenchers to produce quantitative, regiospecific elimination (production of *exo* olefin) at the living PIB chain end was discovered by us during a quenching study involving pyrrole and its derivatives. The expected reaction was alkylation of the pyrrole derivative by the PIB carbenium ion via electrophilic aromatic substitution, and indeed this was the observed reaction

Table 2.
Polyisobutylene End-Group Composition from Di-*tert*-Butyl Sulfide Quenching.

Entry	Base	[D*t*BS]/[CE]	Term. Temp.[a] (°C)	PIB End-Group Composition (mol %) Determined using ^{1}H NMR				
				exo-olefin	*endo*-olefin	Coupled	^{t}Cl	Ether
1	TEA	4.0	−60	100.0	0.0	0.0	0.0	0.0
			−20	100.0	0.0	0.0	0.0	0.0
2	–	4.0	−60	100.0	0.0	0.0	0.0	0.0
			−20	100.0	0.0	0.0	0.0	0.0
3	TEA	1.5	−60	100.0	0.0	0.0	0.0	0.0
			−20	100.0	0.0	0.0	0.0	0.0

Hex/MeCl = 60/40 (v/v); [IB] = 1.5 M; [CE] ≅ [TMPCl] = 0.039 M; [26Lut] = 0.005 M; $[TiCl_4]$/[CE] = 4.0; [TEA]/[CE] = 1.2.
[a] Polymerization and quenching temperature = −60°C; reaction was slowly warmed and aliquots were terminated with excess methanol at the indicated temperature.

with pyrrole itself and with *N*-methylpyrrole.[26] However, 2,5-dimethylpyrrole (25DMP) unexpectedly yielded quantitative *exo* olefin.[22] Although we later showed that quenching by 25DMP proceeds by a unique mechanism[27] (as discussed in the next section), this initial discovery led us to identify a number of hindered base quenchers that were effective for production of *exo*-olefin PIB by *in-situ* quenching.

The range of useful hindered base quenchers is shown in Figure 1. When introduced into a cationic polymerization, these compounds typically undergo a reversible 1:1 complexation with Lewis acid; however, the position of the complexation equilibrium is sensitive to steric crowding around nitrogen. As originally proposed by Faust,[28] free base can exist in sufficient concentration to cause elimination at the chain end if the compound is sterically too hindered to quantitatively complex with $TiCl_4$ but sufficiently sterically unhindered to still allow approach to the carbenium ion. As shown in Figure 1, di-*tert*-butylpyridine (DTBP) is so sterically hindered that it can neither complex with Lewis acid nor approach the carbenium ion and thus represents one extreme. In contrast, 2,6-lutidine (26Lut) is sufficiently sterically unhindered that it is complexed quantitatively with Lewis acid and thus represents the other extreme. Compounds with an intermediate degree of steric crowding such as 1,2,2,6,6-pentamethylpiperidine (PMP) and 2,2,6,6-tetramethylpiperidine (TMP) were found to work very well.

Hindered base quenchers produce *exo*-olefin PIB by the mechanism shown in Figure 2. Reaction **1** is the ionization equilibrium of the living PIB chain end, and Reaction **2** is the complexation equilibrium between quencher and Lewis acid, characterized by the equilibrium constant K_{com}. Complexation of the quencher with $TiCl_4$ is incomplete due to steric hindrance, resulting in a finite concentration of free base in solution. Reaction **3** is the actual E2 elimination reaction, in which the free base regio-specifically abstracts a β-proton from the PIB carbenium ion to produce exclusively *exo*-olefin chain ends. The hindered base may be regenerated if a fully complexed base such as 2,6-lutidine is present and capable of acting as a proton sink (Reaction **4**). Reaction **5** is coupling of two PIB chains, which is a side-reaction, generally undesired, that occurs when the E2 elimination reaction is relatively slow.

From a consideration of Reactions **1**, **2**, and **3**, the following first-order, integrated expression for the rate of quenching may be derived,[27] provided that the concentrations of $TiCl_4$ and free quencher, [Q], remain constant (psuedo-first-order conditions) and assuming near-complete complexation of the quencher ($1 << K_{com}[TiCl_4]$).

$$-\ln(1-p) = k_{-H}\frac{K_{eq}}{K_{com}}[TiCl_4]_{effective}[Q]_o t \quad (1)$$

The effective $TiCl_4$ concentration is approximately $[TiCl_4]_{effective} \cong [TiCl_4]_o - [26Lut] - [Q]_o$, where $[TiCl_4]_o$ and $[Q]_o$ are the nominal concentrations of Lewis acid and quencher charged to the reactor, p is the fractional conversion of living chain ends to *exo* olefin, and [26Lut] is the

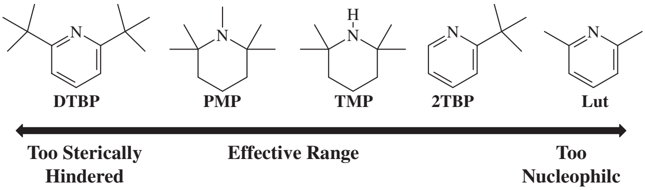

Figure 1.
Effective range of hindered based quenching in relation to steric hindrance around nitrogen.

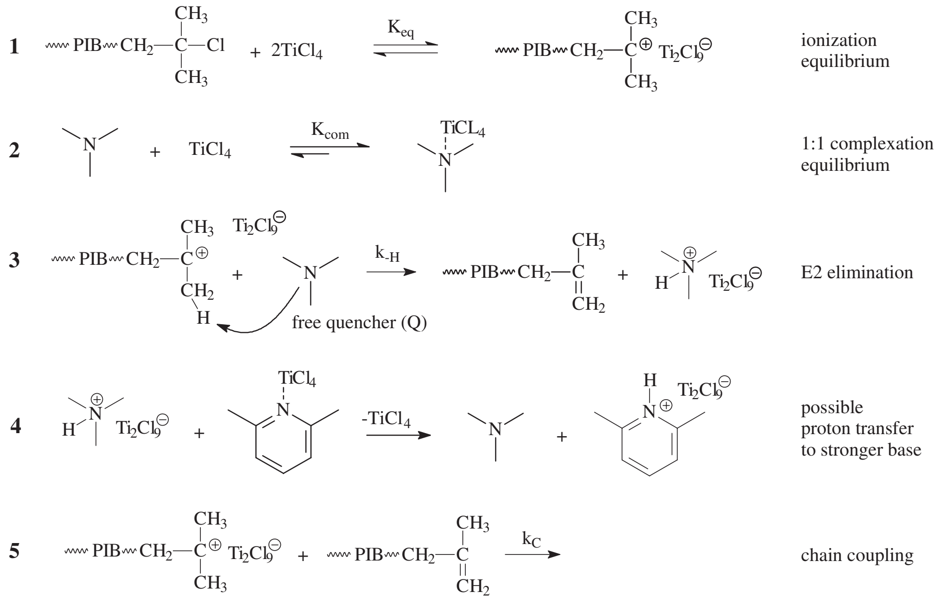

Figure 2.
Mechanism of *exo*-olefin formation using hindered base quenchers.

concentration of the proton trap/common ion salt precursor, 2,6-lutidine, used during IB polymerization. Figure 3(a) shows that first-order quenching kinetics were indeed observed (concordance with eq 1) when $TiCl_4$ was provided in large excess relative to chain ends, i.e, $[TiCl_4]_o = 25 \times [CE]$, and conversion was limited. Similar first order plots were obtained for various hindered base quenchers and for 25DMP.

Introducing the above definition of $[TiCl_4]_{effective}$ into eq 1 yields the following:

$$-\ln(1-p) = k_{\text{-H}}\frac{K_{eq}}{K_{com}}\left\{\left([TiCl_4]_o\text{-}[Lut]\right)[Q]_o\text{-}[Q]_o^2\right\}t \qquad (2)$$

Eq 2 predicts that, with increasing $[Q]_o$, the rate of quenching rises linearly at low $[Q]_o$,

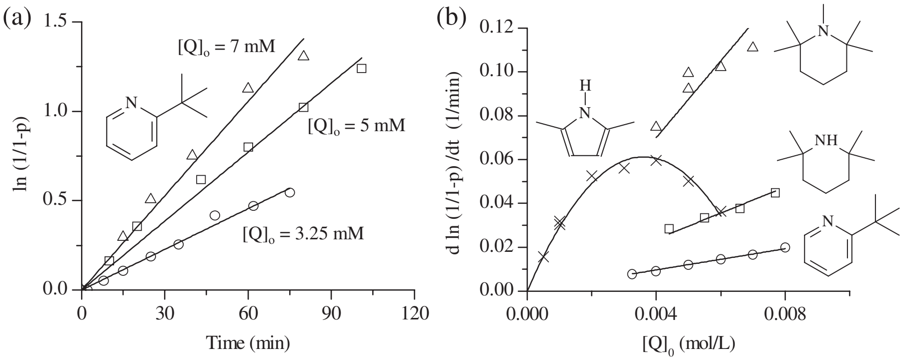

Figure 3.
(a) First-order kinetics plots for quenching living PIB with 2-*tert*-butylpyridine. −60°C; 60/40 Hex/MeCl (v/v); $[CE] = 0.001\,M$, $[26Lut] = 0.005\,M$, $[TiCl_4]_o = 0.025\,M$. (b) Apparent rate constant for quenching vs. the nominal quencher concentration, $[Q]_o$. −60°C; 60/40 Hex/MeCl (v/v); $[CE] = 0.001\,M$, $[26Lut] = 0.005\,M$, $[TiCl_4]_o = 0.025\,M$. 25DMP (×), 2TBP (○), TMP (□) and PMP (Δ).

reaches a maximum, and eventually falls (a parabolic dependence on $[Q]_o$). As more quencher is used, the rate initially increases due to higher amounts of free quencher; however, the rate is simultaneously retarded due to a decrease in available $TiCl_4$ due to complexation with the quencher. A maximum rate is predicted at $[Q]_o = ([TiCl_4]_o - [26Lut])/2$. Figure 3(b) plots the observed first-order rate constants for the various quenchers as a function of nominal quencher concentration. For 2TBP, TMP, and PMP the plotted data are more or less linear, monotonically increasing over the range of 4 to 8 equiv per chain end. In contrast, the observed first-order rate constant for 25DMP is proportional to nominal quencher concentration only at low quencher concentrations; it then reaches a maximum and finally decreases with increasing concentration. However, under these conditions eq 2 predicts a maximum at $[Q]_o = 0.01$ M; the significantly earlier maximum for 25DMP was one of the initial findings that suggested a significant difference in the quenching mechanism of 25DMP compared to the general hindered base quenchers.

Eq 1 predicts that the rate of quenching should display a first-order dependency on $[TiCl_4]_{effective}$. This prediction was confirmed by experiment.[27]

N-Hydro-2,5-disubstitutedpyrrole Quenchers

As discussed in the last section 2,5-dimethylpyrrole (25DMP) was the first hindered base quencher to be discovered, but it soon became clear that it operated by an entirely different mechanism than the general hindered base quenchers exemplified by the pyridines and piperidines. It was also discovered that 2,3,4,5-tetramethylpyrrole behaves nearly identically to 25DMP,[29] but that 1,2,5-trimethylpyrrole[29] and 2,4-dimethylpyrrole[30] do not, suggesting that the pyrrole must be an *N*-hydro-2,5-disubstitutedpyrrole for this unique quenching behavior to occur. In our attempts to understand the quenching mechanism for *N*-hydro-2,5-disubstituted-pyrroles, we knew that any proposed model must comport with the following experimental observations:

- Concentration of free quencher, [Q], must be nearly equal to the nominal concentration of added quencher, $[Q]_o$.
- Reaction of quencher with $TiCl_4$ must throw a precipitate, but this process must not reduce the effective concentration of the active quenching species.
- Rate of quenching must display a second order dependence on $[TiCl_4]_{effective}$.
- Rate of quenching must rise through a maximum and then fall with increasing $[Q]_o$.

The first two requirements above suggested that the *N*-hydro-2,5-disubstituted-pyrrole was reacting exhaustively with excess $TiCl_4$ to produce the true quenching species plus some insoluble by-product. The mechanism shown in Figure 4 satisfies all four observations above and identifies the true quenching species to be the η^5-2,5-disubstituted-pyrrolyltrichlorotitanium(IV) coordination complex. The participation of a strong tertiary amine base, such as 2,6-lutidine, as an ultimate proton acceptor is integral to the mechanism and generally necessary for the production of 100% *exo*-olefin PIB when using a *N*-hydro-2,5-disubstitutedpyrrole quencher.

To lend support to this mechanism, we isolated the η^5-2,5-disubstituted-pyrrolyltrichlorotitanium(IV) complex in C_6D_6 solution and characterized it using ^{1}H and ^{13}C NMR.[27] Figure 5 shows the resulting ^{13}C NMR spectrum.

According to the mechanism in Figure 4, the concentration of the active quencher, $Ti(\eta^5\text{-25DMP})Cl_3$, is equivalent to the concentration of *N*-hydro-2,5-disubstituted-pyrrole charged to the reactor. Consequently, the correct form of eq 1 for a *N*-hydro-2,5-disubstitutedpyrrole is the following,

$$-\ln(1-p) = k_{-H}K_{eq}[TiCl_4]^2_{effective}[Q]_o t \tag{3}$$

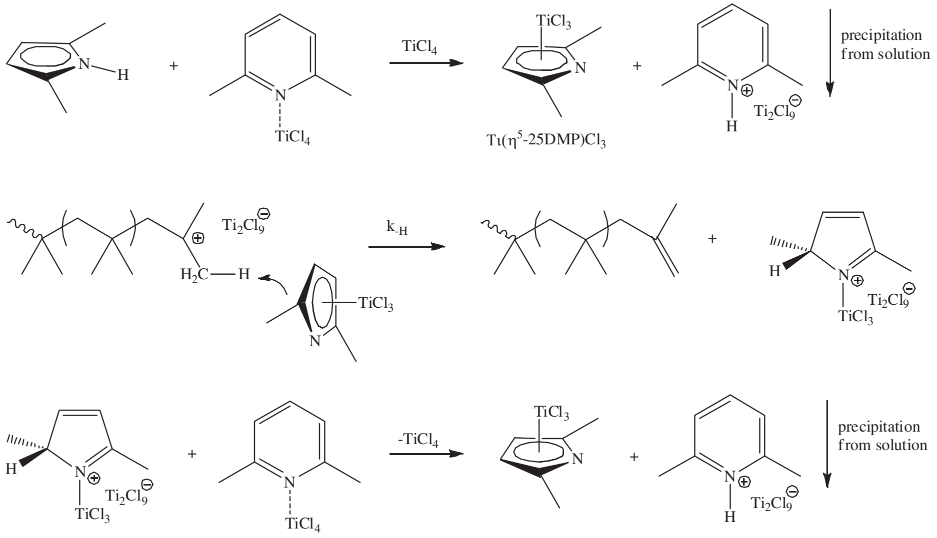

Figure 4.
Mechanism of *exo*-olefin formation using *N*-hydro-2,5-disubstitutedpyrrole quenchers in the presence of excess strong base, *e.g.*, 2,6-lutidine.

where, $[TiCl_4]_{effective} = [TiCl_4]_o - [26Lut] - 2[Q]_o$. The coefficient of 2 on $[Q]_o$ accounts for the fact that a net consumption of two molecules of $TiCl_4$ occurs for every $Ti(\eta^5\text{-}25DMP)Cl_3$ complex formed, when $[26Lut] > [Q]_o$. When the above definition of $[TiCl_4]_{effective}$ is introduced into eq 3, and the differential, $d(-\ln(1\text{-}p)/dt$, is set to zero, we find that the maximum rate of quenching is predicted at a value of $[Q]_o$ much lower than that predicted for hindered base quenching, namely, $[Q]_o = ([TiCl_4]_o - [26Lut])/6$. Under the conditions of Figure 3(b), the predicted maximum is $[Q]_o = 3.3 \times 10^{-3}$ M, which is approximately equal to the observed maximum for 25DMP in the figure.

Eq 3 predicts that the rate of quenching should display a second-order dependency on $[TiCl_4]_{effective}$. This prediction was confirmed by experiment.[27]

Sulfide, Ether, and Silylether Quenchers

The mechanism of operation of this class of quenchers is well understood only for sulfides; however, it is likely to be similar for ethers and silylethers. The sulfide quenching mechanism is shown in Figure 6. Upon addition of a sulfide to quasiliving PIB, the chain ends are quantitatively converted to the corresponding sulfonium ion.[24] At this point, destruction of the catalyst by addition of a protic nucleophile, *e.g.*, methanol, generally

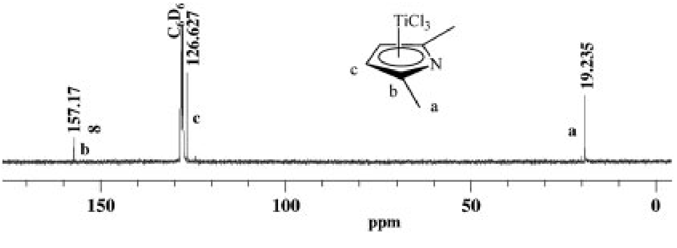

Figure 5.
^{13}C NMR (75 MHz, C_6D_6, 22°C) spectrum of $Ti(\eta^5\text{-}2,5\text{-dimethylpyrrolyl})Cl_3$.

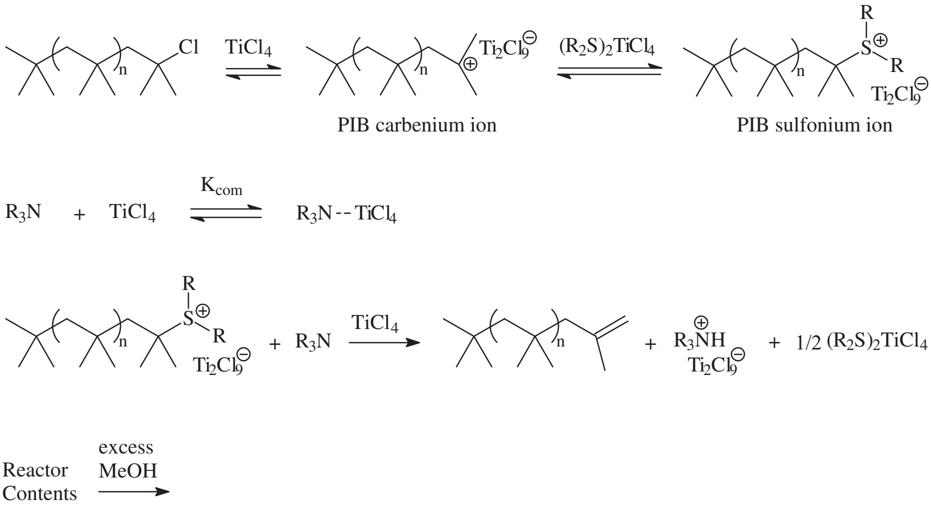

Figure 6.
Mechanism of *exo*-olefin formation using sulfide quenchers.

results in a mixture of products including predominantly *exo*-olefin but also possibly *endo*-olefin, *tert*-chloride, methyl ether, and coupled PIB. However, addition of a base such as a tertiary amine can result in nearly quantitative *exo*-olefin PIB, provided a sufficient concentration of free base (non-complexed with the Lewis acid) can be achieved in the reaction mixture. For simple, non-hindered bases such as TEA, this is most easily accomplished by raising the temperature, *e.g.*, to –20°C, in order to shift the complexation equilibrium (second step in Figure 3) to the left.

The effect of sulfide structure and termination temperature on PIB end-group composition is summarized in Table 1. Increasing yield of *exo*-olefin end groups was observed in the approximate order of increasing bulkiness of the substituent on the sulfide, i.e., *n*-alkyl << isopropyl < *tert*-butyl. For the *n*-alkyls, the fraction of *tert*-chloride end groups increased as the length of the alkyl group increased from methyl to *n*-butyl. Increasing termination temperature increased the yield of *exo*-olefin, but the effect was significant only for diisopropyl sulfide. The most noteworthy finding in Table 1 was the extraordinary effectiveness of di-*tert*-butyl sulfide, which yielded 100% *exo*-olefin-terminated PIB with no other detectable end groups within the sensitivity limitation of 300 MHz ^{1}H NMR, irrespective of the termination temperature.

Experiments were conducted to further explore quenching reactions involving di-*tert*-butyl sulfide (Table 2). Entries 1 and 2 are identical except that the base TEA was omitted from Entry 2. The latter experiment resulted in 100% *exo*-olefin end groups irrespective of the methanol termination temperature, demonstrating that addition of a base is unnecessary with D*t*BS quenching. The mechanism by which elimination occurs in the absence of a base is thought to be E2 elimination by methanol. Apparently, with D*t*BS, steric strain in the sulfonium cation is so great that regiospecific E2 elimination is the only reaction observed, even with weak bases such as alcohols. Comparison of Entries 1 and 3 in Table 2 shows that with D*t*BS, the quencher/chain end ratio can be reduced downward toward 1:1 without apparent harm to the yield of *exo*-olefin functionality.

Table 3 demonstrates the preparative capability of sulfide and ether quenching. For any of the quenching methods designed

Table 3.
Preparative Capability of Sulfide and Ether Quenching.

[CE] (M)	Quencher	[Q]/[CE]	[$TiCl_4$]/[CE]	PIB End-Group Composition (mol %) Determined using ^{1}H NMR			
				exo-olefin	*endo*-olefin	Coupled	*tert*-Cl
0.10	di-*t*-Butyl sulfide	2.0	2.2	100.0	0.0	0.0	0.0
0.10	Diisopropyl Ether	4.0	4.0	100.0	0.0	0.0	0.0

Hex/MeCl = 60/40 (v/v); initiator = TMPCl; [IB] = 3.87 M; [26Lut] = 0.005 M. Quenching and termination (MeOH) temp. (sulfide) = −60°C. Quenching and termination (MeOH) temp. (ether) = −70°C.

to produce *exo*-olefin PIB, coupled PIB can potentially be a significant side product. This is especially true for hindered base quenchers,[22] since PIB carbenium ion and *exo*-olefin product co-exist during the quenching reaction. Coupling can be largely avoided with sulfide (and ether) quenching because the living PIB chain ends are first quantitatively converted to the more stable PIB sulfonium ion[24] (oxonium ion presumably in the case of the ether), which has no tendency to react with the *exo*-olefin product. However, since coupling is bimolecular in chain ends, any slight tendency toward coupling, however insignificant at low [CE], is expected to increase with the square of the chain end concentration. Table 3 shows that both sulfide and ether quenching are exceptionally resistance to the formation of coupled PIB. Both methods yield 100% *exo* olefin, even under highly concentrated conditions of [CE] = 0.1 M.

Comparison of Quenching Methods

A comparison of the various *exo*-olefin quenching methods is presented in Table 4. Many of the reactions were carried out at [CE] = 0.077 M, which provides a useful comparison of the various methods at a moderately high chain end concentration.

25DMP yielded a high fraction of *exo*-olefin chain ends only in the presence of high [$TiCl_4$] and [26Lut], and it failed to yield 100% *exo*-olefin, except under very dilute conditions, i.e., [CE] = 0.014 M. The high demand for $TiCl_4$ and 26-lutidine with 25DMP quenching is a consequence of the

Table 4.
Comparison of Various Quenching Methods Toward *Exo*-Olefin Polyisobutylene.

Quencher	[CE] M	[IB] M	[Q]/[CE]	[$TiCl_4$]/[CE]	[Lut] M	End-Group Composition (mol %) Determined using ^{1}H NMR			
						exo-olefin	*endo*-olefin	Coupled	*tert*-Cl
25DMP	0.014	0.5	1.43	5.93	0.010	100.0	0.0	0.0	0.0
25DMP	0.039	1.5	1.43	5.93	0.005	49.6	1.5	33.2	15.7
25DMP	0.039	1.5	1.43	5.92	0.042	90.5	0.9	4.5	4.1
25DMP	0.039	1.5	2.85	9.63	0.042	84.7	0.8	6.0	8.5
25DMP	0.039	1.5	1.43	7.07	0.103	94.3	0.0	5.7	0.0
PMP	0.014	0.5	2.86	5.93	0.010	100.0	0.0	0.0	0.0
PMP	0.039	1.5	2.85	5.93	0.005	100.0	0.0	0.0	0.0
PMP	0.077	3.0	2.86	5.93	0.005	Forms intractable complex			
D*t*BS	0.039	1.5	4.00	4.00	0.005	100.0	0.0	0.0	0.0
D*t*BS	0.077	3.0	4.00	4.00	0.005	100.0	0.0	0.0	0.0
D*t*BS	0.10	3.87	2.00	2.2	0.005	100.0	0.0	0.0	0.0
DIPE	0.039	1.5	4.00	4.00	0.005	100.0	0.0	0.0	0.0
DIPE	0.10	3.87	4.00	4.00	0.005	95.3	0.9	3.8	0.0
DIPE[a]	0.10	3.94	4.00	4.00	0.005	100.0	0.0	0.0	0.0
EtOTMS	0.039	1.5	4.00	4.00	0.005	98.0	2.0	0.0	0.0
MATMS	0.039	1.5	2.80	1.67	0.005	100.0	0.0	0.0	0.0
MATMS	0.077	3.0	2.80	1.67	0.005	97.0	1.0	2.0	0.0

−60°C; Hex/MeCl = 60/40 (v/v); initiator = TMPCl.
[a] −70°C.

mechanism shown in Figure 3. Formation of the active coordination complex consumes 3 equivalents of $TiCl_4$ and one equivalent of 26Lut per equivalent of 25DMP used, plus an additional 2 equivalents of $TiCl_4$ and one equivalent of 26Lut are consumed per equivalent of PIB chain end converted to *exo* olefin. PMP proved to be considerably more effective, and efficient, than 25DMP, yielding 100% *exo*-olefin at [CE] = 0.039 M with only moderate [$TiCl_4$] and no additional [26Lut] beyond that routinely used for the prior cationic polymerization. These observations are consistent with the mechanism for hindered base quenching shown in Figure 2. PMP is a stronger base than 26-lutidine, and therefore retains the proton after the E2 reaction at the chain end; 2,6-lutidine essentially plays no role in the quenching process. Two equivalents of $TiCl_4$ per equivalent of PIB chain end are still required to form the counteranion to the resulting 1,2,2,6,6-pentamethylpiperidinium cation. PMP did eventually fail as the system was further concentrated, surprisingly due to a physical rather than a kinetic limitation. At [CE] = 0.077 M, the $TiCl_4$-PMP complex formed an intractable solid precipitate that rendered further mixing of the reactor contents impossible.

Bulky sulfides and ethers, specifically di-*tert*-butyl sulfide (D*t*BS) and diisopropyl ether (DIPE), were the most effective *exo* olefin producing quenchers studied. Both yielded 100% *exo* olefin, even under very concentrated conditions of [CE] = 0.10 M. The ether, however, had to be used in greater excess relative to chain ends, 4x vs. 2x for the sulfide, and it required a slightly lower temperature, −70°C vs. −60°C for the sulfide. A significant advantage of the ether relative to the sulfide is absence of odor; D*t*BS has a disagreeable odor, typical of sulfur-containing compounds.

A representative silyl ether, ethoxytrimethylsilane (EtOTMS) was also included in Table 4 for comparison. It yielded 98% *exo* olefin/2% *endo* olefin with no other end group types detected, at [CE] = 0.039 M.

Methallyltrimethylsilane (MATMS) was also examined as a comparative quenching method. It yielded 100% *exo*-olefin at [CE] = 0.039 M, but only yielded 97% *exo*-olefin under the more difficult conditions of [CE] = 0.077 M.

Figure 7 shows a representative ^1H NMR spectrum of *exo*-olefin PIB produced at high chain-end concentration. This particular sample was produced using DIPE as the quencher at −70°C, with [CE] = 0.10 M. The spectrum shows only one species of end group, namely *exo* olefin with characteristic peaks at 4.64 and 4.85 ppm. Noteworthy is the complete absence of *endo* olefin at 5.15 ppm, coupled PIB olefin at 4.82, and *tert*-chloride end groups at 1.68 ppm.

Conclusion

A number of different *in situ* quenching methods have been developed to yield *exo*-olefin PIB in a convenient manner directly from $TiCl_4$-co-initiated living polymerizations. *N*-Hydro-2,5-disubstitutedpyrroles and hindered base quenchers such as the sterically hindered piperidines, operate by direct E2 elimination at the PIB carbenium ion. These classes of quenchers are consequently less effective at higher chain-end concentrations due to reaction of the PIB carbenium ion with *exo*-olefin product to yield coupled PIB. They also tend to form insoluble complexes with $TiCl_4$ that can cause physical mixing problems in the reactor.

Bulky sulfides and ethers are the highest performing and most effective classes of quenchers. They operate by converting the PIB chain ends quantitatively into the corresponding onium ions. Then, under proper conditions, the adduct can be decomposed to yield *exo* olefin. This process prevents the coexistence of carbenium ions and *exo*-olefin product within the reactor, and thus coupling is greatly reduced or eliminated. Since onium ion formation is reversible, with an equilibrium that is dependent on quencher structure, the various quenchers must be employed at different concentrations to achieve quantitative onium ion formation. Moreover, only

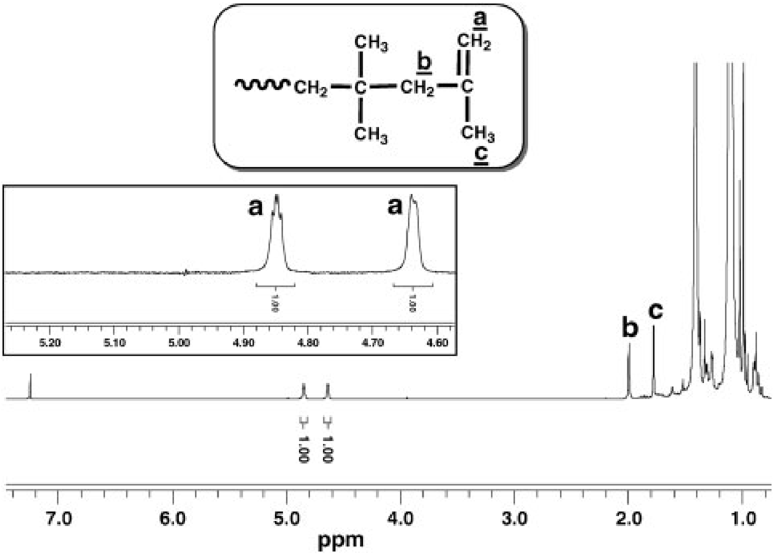

Figure 7.
^{1}H NMR spectrum of *exo*-olefin-terminated PIB obtained by quenching living PIB with diisopropyl ether (DIPE). $-70\,^\circ$C; Hex/MeCl 60/40 (v/v); [TMPCl] = 0.10 M; [IB] = 3.94 M; [DIPE]/[CE] = 4.00; [$TiCl_4$]/[CE] = 4.00; [Lut] = 0.005 M.

bulky onium ions decompose to yield 100% *exo* olefin. Di-*tert*-butylsulfide is arguably the best among all of the quenchers studied, in terms of performance and economy (low quencher and $TiCl_4$ demand); diisopropyl ether is an excellent alternative with the advantage of no odor.

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