Carbocation Rearrangement in Controlled/Living Isobutylene Polymerization

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ABSTRACT: Isobutylene polymerization was initiated using the cumyl chloride/$TiCl_4$/2,4-dimethylpyridine system ([IB] = 1.0 M, [CumCl] = 2.3×10^{-2} M, [$TiCl_4$] = 0.24 M, [DMP] = 2.4×10^{-3} M). Polymerization kinetics in 60/40 hexane/MeCl at −80 °C showed that an IB conversion of ~98% was reached in 70 s. The active centers were monitored over time at high conversion, by ^1H NMR after quenching with MeOH or allyltrimethylsilane (ATMS), and by GPC after a second addition of IB. Quenching with MeOH or ATMS at times up to 70 s yielded quantitative *tert*-chloride or allyl chain ends, respectively. For longer periods up to 12 h, MeOH-quenched PIB showed increasing depletion of *tert*-chloride chain ends of the normal structure (but no appearance of olefin) and ATMS quenching yielded a gradual reduction in allylation to 78% at 12 h. Real-time ^1H NMR of an active polymerization mixture also indicated depletion of *tert*-chloride end groups. GPC results showed that coupling of PIB chains was not occurring and that a second charge of IB was slowly initiated. The latter process caused a fraction of the chain ends to be restored with normal *tert*-chloride groups. It was hypothesized that normal *tert*-chloride chain ends slowly undergo carbenium ion rearrangement to form a mixture of isomerized chain end structures. This process represents the dominant chain interrupting event in $TiCl_4$-co-initiated IB polymerization under these conditions. The rearranged structures were hypothesized to result from combinations of 1,2-hydride and 1,2-methide shifts; ^1H NMR analysis of a dehydrochlorinated sample was consistent with this interpretation. The rate of depletion of *tert*-chloride end groups was shown to follow first-order kinetics with an apparent rate constant of 8×10^{-5} s^{-1}. The ratio of rate constants for propagation and rearrangement, k_p/k_r, was calculated to be 3×10^4 M^{-1}.

Introduction

The stability of the propagating species in controlled/living polymerizations is a topic of great fundamental and technological importance,[1−3] and this issue has been discussed for the case of carbocationic polymerizations in several recent papers.[4,5] Stability is best defined as resistance to chain transfer and termination reactions, quantified by the ratios $k_p/k_{tr,M}$ and k_p/k_t, where k_p is the rate constant for propagation and $k_{tr,M}$ and k_t are the rate constants for bimolecular chain transfer to monomer and unimolecular termination, respectively. These quantities determine the highest molecular weight that can be ultimately attained from a given system, while at the same time maintaining the propagating activity of an acceptable fraction of the original number of chains.

Controlled/living carbocationic polymerizations are characterized by an ionization equilibrium between active and reversibly deactivated (dormant) chains. For example, in the polymerization of isobutylene (IB) activated by $TiCl_4$ or BCl_3, a small concentration of carbenium ions exists in equilibrium with a much larger concentration of *tert*-chloride terminated chains. The lower the effective ionization equilibrium constant, the greater is the amount of time that is available for synthetic manipulations such as linking and in situ functionalization, and thus the shelf life of the system is extended.[6] For $TiCl_4$-activated systems, the exact form of the equilibrium expression may vary since the kinetic order of the rate of polymerization with respect to $TiCl_4$ has been observed to be either first[7] or second[8,9] depending upon conditions.

Many researchers have reported the controlled/living polymerization of IB at relatively high initiator concentrations, but few reports have addressed the limits of livingness of polyisobutylene (PIB) under conditions of high [M]/[I] and/or high monomer conversion. It has become apparent that livingness of IB polymerization systems co-initiated by $TiCl_4$ at low temperature (i.e., −80°) is limited not by chain transfer to monomer but rather by a unimolecular termination process. Under certain conditions, this is evidenced by downward curvature of first-order kinetic plots at high monomer conversions but with perfect linearity in molecular weight vs monomer conversion plots.[10] Conventional wisdom holds that unimolecular termination should involve β-proton expulsion to produce terminal unsaturations; however, these have not been observed. Nonetheless, it has been observed that, at very high monomer conversion, the normal *tert*-chloride chain ends of PIB gradually become depleted. This paper reports a study of the structure and reactivity of the propagating end groups in controlled/living IB polymerization at very high monomer conversion, i.e., under monomer starvation conditions, in the presence of an active Lewis acid with the goal of characterizing the dominant termination process in these systems.

Experimental Section

Cumyl chloride (CumCl) was prepared by bubbling HCl through neat α-methylstyrene at 0 °C. The product was passed through a column of anhydrous $MgSO_4$ and $NaHCO_3$ just before use. ATMS (Aldrich Chemical Co.) was vacuum distilled from CaH_2 prior to use. Hexane-d_{14} was used as received from Aldrich Chemical Co. The source and preparation of other reagents have been previously described.[8,9]

Isobutylene polymerizations were initiated using the CumCl/$TiCl_4$/2,4-dimethylpyridine system ([IB] = 1.0 M, [CumCl] = 2.3×10^{-2} M, [$TiCl_4$] = 0.24 M, and [DMP] = 2.4×10^{-3} M) at

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Table 1. Polymerization Conditions and GPC Results for IMA Experiments

sample	reaction time	incremental addition	reaction time after addition (min)	M_n[c]	M_w/M_n[c]	M_n (theoretical)[d]
a	70 s	5 mL of MeOH		2340	1.45	2600
b	12 h	5 mL of MeOH		2390	1.50	2600
c	70 s	20 mL of soln 1[a]	6	12000	1.12	13000
d	12 h	20 mL of soln 1	2	bimodal		13000
e	12 h	20 mL of soln 1	4	bimodal		13000
f	12 h	20 mL of soln 1	6	bimodal		13000
g	12 h	20 mL of soln 2[b]	6			3200

[a] Solution 1: 27 mL of MeCl; 41 mL of hexane; 0.875 mol of IB. [b] Solution 2: 69 mL of MeCl; 104 mL of hexane; 0.063 mol of IB. [c] GPC with multi-angle laser light scattering detector.[12] [d] Assuming essentially complete IB conversion.

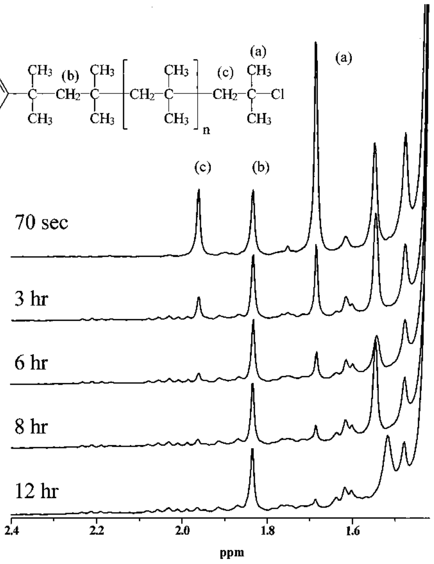

Figure 1. ^{1}H NMR spectra (1.5−2.4 ppm region) of PIB quenched at the indicated time by MeOH.

−80 °C under dry N_2 gas within an inert-atmosphere glovebox. These conditions were chosen to provide a degree of polymerization (DP) of 43, and nearly complete IB conversion in about 1 min. The procedure was as follows: to a 1 L three-necked flask equipped with mechanical stirrer were added 312 mL of MeCl, 3.149 g of CumCl, 468 mL of hexane, 0.852 mol of IB, and 2.2×10^{-3} mol of DMP. (In one series of experiments, DMP was either eliminated from the recipe altogether, or was substituted by an equimolar quantity of either di-*tert*-butylpyridine, pyridine, or octyl *p*-(dimethylamino)benzoate.) The resulting masterbatch solution was stirred for 30 min, and then 16−50 mL aliquots were transferred into separate 25 × 200 mm culture tubes. Each tube was initiated by the addition of 1.19×10^{-2} mol of $TiCl_4$ (neat and at room temperature). Pairs of tubes were quenched at various reaction times up to 12 h (see Figure legends); one of the pair received 5 mL of prechilled MeOH, the other 6.0×10^{-3} mol of allyltrimethylsilane (ATMS). After quenching, the contents of each tube were poured into a tared 16 oz jar containing 50 mL of MeOH at 23 °C. After evaporation of most of the solvents, the remaining liquid was decanted from the precipitated polymer. The latter was redissolved by addition of 10 mL of hexane and then reprecipitated by addition of 250 mL of MeOH. The supernatant liquid was decanted, and the precipitation procedure was repeated. The jars were placed in a vacuum oven at 23 °C until constant weight was observed. The apparent rate constant for propagation was obtained from a plot of ln([M]$_0$/[M]) vs time, where [M]$_0$/[M] was calculated from the fractional yield. Structure and reactivity of the active centers were assessed from ^{1}H NMR spectra of the as-isolated polymers and of selected polymers which were subjected to dehydrochlorination, performed according to the method of Kennedy et al.[11]

Gel permeation chromatography (GPC) was used to analyze the effect on polymer molecular weight and molecular weight distribution (MWD) of a second increment of IB monomer. This was carried out by first preparing a polymerization masterbatch as described above and transferring 30 mL aliquots into each of seven culture tubes. Each tube was initiated by the addition of 7.0×10^{-3} mol of $TiCl_4$. Two of the tubes were allowed to react for 70 s and the rest for 12 h. After reaching their respective polymerization times, each tube received either 5 mL of prechilled MeOH or a 20 mL aliquot of one of two IB-containing solutions, as outlined in Table 1. Tubes receiving solutions of IB were allowed to further react for the indicated time before the addition of 5 mL of prechilled MeOH. Solution 1 contained 27 mL of MeCl, 41 mL of hexane, and 0.875 mol of IB; solution 2 comprised 69 mL of MeCl, 104 mL of hexane, and 0.063 mol of IB. Polymer isolation was performed as described above. GPC procedure and instrumentation have been described.[12]

Real-time ^{1}H NMR analysis was performed at −78 °C as follows: to a prechilled 10 mL graduated cylinder were charged 1.46×10^{-4} mol of 1,3-bis(2-chloro-2-propyl)-5-*tert*-butylbenzene (*t*Bu-*m*-DCC), 1.1 mL of methylene chloride ($MeCl_2$), 2.2 mL of hexane-d_{14}, 3.2×10^{-3} mol of IB, and 7.0×10^{-6} mol of DMP. The solution was gently swirled for 30 min to ensure complete mixing. Polymerization was initiated by the rapid injection of 2.9×10^{-3} mol of $TiCl_4$ (neat and at room temperature). The solution was gently swirled to ensure homogeneity, and then 2 mL of the reacting mixture was transferred to a prechilled 5 mm o.d. NMR tube equipped with a PTFE-lined screw cap. During transfer to the spectrometer, the NMR tube was maintained at −78 °C by immersion in 30 mL of $MeCl_2$ contained within a test tube cooled by solid CO_2/acetone. The NMR tube was quickly placed in a ceramic spinner, and positioned appropriately in the 300 MHz spectrometer. The probe temperature was maintained at −78 °C for 7 h, and spectra (32 scans) were recorded every 30 min.

^{1}H NMR spectra of polymers were acquired on a Bruker AC-300 spectrometer using 5 mm o.d. tubes and sample concentrations of 5−25% (w/v) in $CDCl_3$ or CD_2Cl_2. The quantity $[P-t\mathrm{Cl}]_0/[P-t\mathrm{Cl}]$ was calculated according to

$$\frac{[\mathrm{P}-t\mathrm{Cl}]_0}{[\mathrm{P}-t\mathrm{Cl}]} = \frac{\mathrm{B}}{\mathrm{A}}\,\frac{\mathrm{A}_0}{\mathrm{B}_0} \qquad (1)$$

where *A* represents the integrated peak area of either the dimethyl (1.67 ppm) or the methylene protons (1.96 ppm) adjacent to the *tert*-chloride end group, *B* represents the integrated peak area of the methylene protons (1.84 ppm) adjacent to the initiator residue, and the zero subscript refers to the quantity measured at 70 s.

Results and Discussion

Structure and Reactivity of PIB Chain Ends as a Function of Aging. Under the conditions used herein, the apparent first-order rate constant, k_{app}, for IB polymerization was measured to be 5.3×10^{-2} s^{-1}, indicating ~98% IB conversion in 70 s. Figure 1 shows ^{1}H NMR spectra (1.5−2.4 ppm region) of PIBs quenched at various times with MeOH. All PIBs that were quenched within 80 s yielded quantitative *tert*-chloride

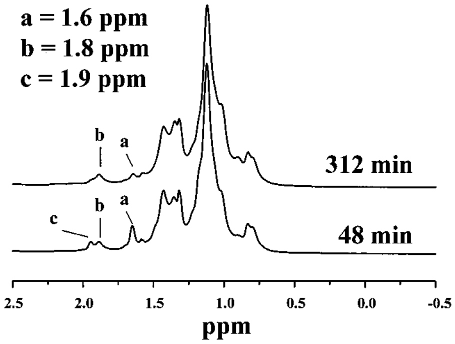

Figure 2. Real-time ^{1}H NMR spectra (−0.5−2.5 ppm region) of IB polymerization mixture at 48 and 312 min. $[IB]_0 = 0.9$ M; [*t*-Bu-*m*-DCC] = 4×10^{-2} M; $[TiCl_4] = 0.8$ M; [2,4-DMP] = 2×10^{-3} M.

end groups (structure shown in Figure 1), as demonstrated by the representative sample at 70 s. The resonances at 1.68 ppm (a) and 1.96 ppm (c) are due to the dimethyl and methylene groups, respectively, directly adjacent to the terminal chlorine atom.[13] The resonance at 1.83 ppm (b) is due to the methylene group directly adjacent to the aromatic initiator residue. Integration of either of the former peaks relative to the latter provided a measurement of the *tert*-chloride functionality of the sample. Polymers which were aged for extended periods revealed a steady diminution of the resonances due to the *tert*-chloride groups and the appearance of many new smaller resonances within the range 1.6−2.3 ppm. Thus, the normal *tert*-chloride end groups were gradually transformed into something else during the course of aging in the presence of active Lewis acid. Elimination of HCl did not occur regardless of reaction time, since the 4−6 ppm region of the spectra indicated that the PIBs were all free of unsaturation.

Although the polymer isolation procedure was carefully designed to be mild, it was desirable to confirm that the loss of *tert*-chloride functionality was occurring during polymerization, and not during workup. This was done by acquiring real-time spectra of an active sample within the ^{1}H NMR spectrometer at −78 °C. Figure 2 shows the aliphatic region of spectra (−0.5−2.5 ppm) acquired at 48 and 312 min for a PIB sample initiated from *t*-Bu-*m*-DCC. The dimethyl and methylene resonances at 1.6 and 1.9 ppm were indeed diminished at 312 compared to 48 min, providing strong evidence that the phenomenon under investigation occurs during polymerization. Close scrutiny of the olefinic region of the same spectra (data not shown) showed that β-elimination had not occurred after 312 min, within the limits of detection of the 300 MHz spectrometer.

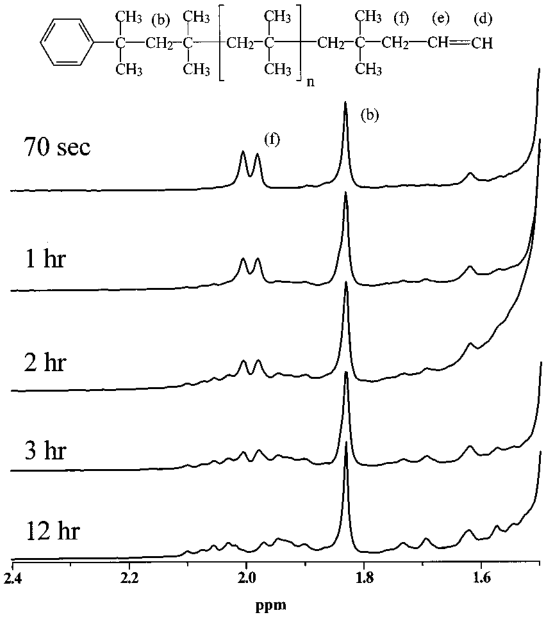

Figure 3. ^{1}H NMR spectra (1.5−2.4 ppm region) of PIB quenched at the indicated time by ATMS.

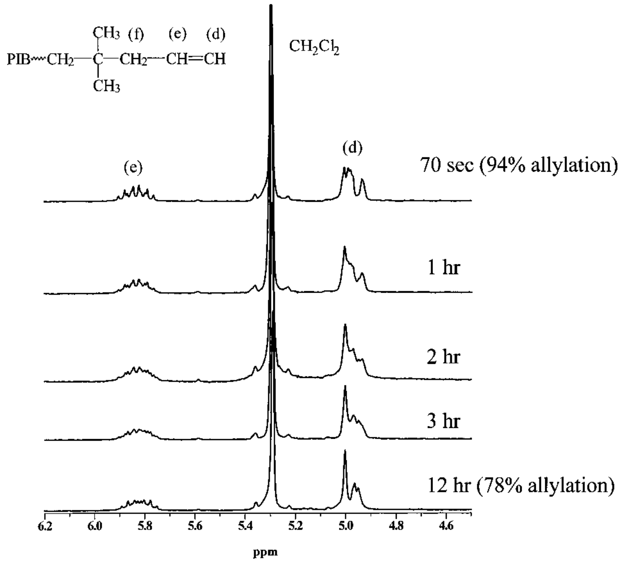

Figure 4. ^{1}H NMR spectra (olefinic region) of PIB quenched at the indicated time by ATMS.

Figures 3 and 4 show the saturated aliphatic and olefinic regions, respectively, of ^{1}H NMR spectra of PIBs which were quenched with ATMS. This reagent has been shown to react with living PIB chains, in situ, to provide terminal allyl functionality.[14] The object was to determine whether the progressive depletion of the *tert*-chloride functional groups observed in Figure 1 would coincide with a progressive failure of the ATMS quenching reaction. As before, the 70 s polymer provided a control spectrum showing the terminal allyl resonances as they typically appear in a PIB sample that is quenched without aging. Figure 3 shows the characteristic doublet centered at 2.0 ppm due to the methylene protons (f). This doublet gradually disappeared with aging and was replaced by a number of smaller doublets with slightly different chemical shifts. Figure 4 shows that the characteristic shape of the multiplet at 5.8 ppm, due to the olefinic methylene protons (d), also changed with aging. The fraction of chains which was allylated was calculated by comparing the total integrated peak area of the olefinic protons in Figure 4 (normalized for three protons) vs the aromatic protons of the CumCl initiator residue (normalized for five protons). These calculations showed that the 70 s polymer was 94% allylated but that the fraction of allylated chains decreased as a function of aging time, to 78% for the 12 h polymer. Nonetheless, it was clear that the fraction of chains which was allylated remained quite large relative to the fraction of chains which retained normal *tert*-chloride functionality. In fact, the latter fraction was too small to be accurately obtained by integration of the ^{1}H NMR spectrum. This implied that the normal *tert*-chloride end groups were trans-

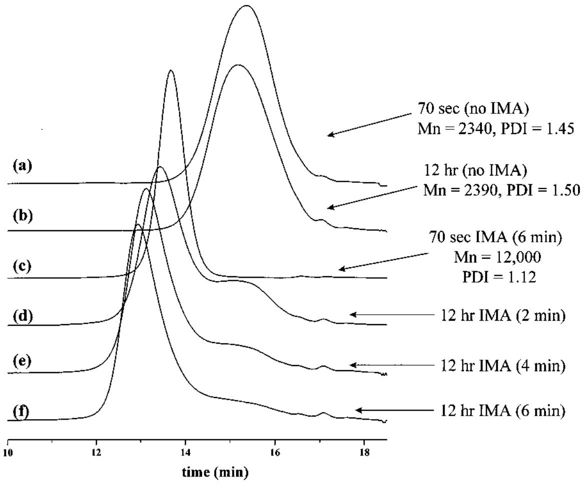

Figure 5. GPC results for aged PIB with and without incremental monomer addition (IMA). Table 1 lists polymerization conditions.

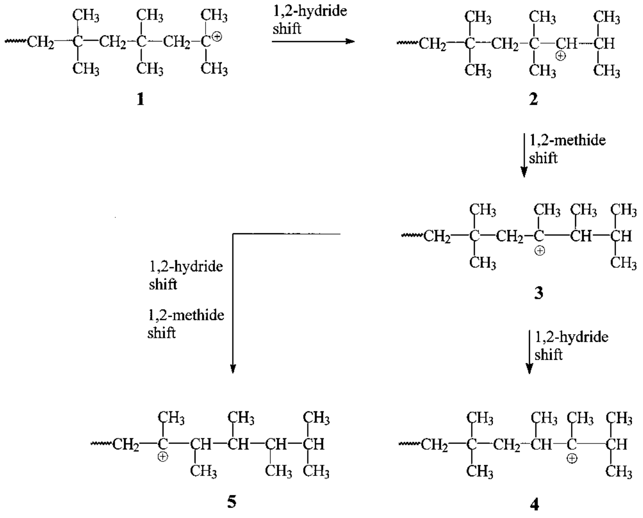

Figure 6. Probable isomerization (rearrangement) pathways for PIB chain ends.

formed into other structures, the majority of which were still active toward ATMS.

Figure 5 and Table 1 show GPC results of incremental monomer addition (IMA) experiments carried out on control and aged PIB samples. Sample a is the 70 s control polymer (no IMA). Its molecular weight is close to theoretical, and although the molecular weight distribution (MWD) is somewhat broad at 1.45, the trace is monomodal and symmetrical. Sample b is the PIB aged for 12 h (no IMA); its molecular weight and MWD are identical with those of the control, indicating that aging has no effect on molecular weight and, in particular, that the *tert*-chloride end groups cannot be disappearing via chain coupling. Sample c was produced by addition of IB to the control polymer at 70 s, followed 6 min later by MeOH quenching. Its molecular weight is close to that calculated based upon the amount of monomer added, and the MWD is significantly more narrow. Samples d−f received a second increment of IB after 12 h aging and were then quenched after an additional 2, 4, and 6 min, respectively. The bimodality of these traces suggests that a fraction of the aged chains failed to reinitiate IB. Diminution of the lower molecular weight peak with polymerization time shows, however, that some of the less reactive chains do slowly initiate and more complete reinitiation would probably be achieved with a larger IB increment and/or longer time. Sample g received a much smaller increment of IB after aging for 12 h. The object was to demonstrate partial reinitiation while keeping the molecular weight low to facilitate end group analysis by ^{1}H NMR spectroscopy. Consistent with the GPC results, analysis showed 24% of the chain ends had been converted back to the normal *tert*-chloride structure.

As a further note, the phenomenon of *tert*-chloride chain end depletion was studied for polymerizations in which the standard basic additive, 2,4-dimethylpyridine, was replaced with either pyridine, 2,6-di-*tert*-butylpyridine, or octyl *p*-(dimethylamino)benzoate or was eliminated entirely. For all polymerizations, with or without an additive, the same depletion of the *tert*-chloride chain ends was observed, and in no case was terminal unsaturation observed due to β-proton elimination.

Rearrangement of PIB Chain Ends. In view of these results, it is proposed that ionized PIB chain ends slowly undergo carbenium ion rearrangements (e.g. hydride and methide shifts) to cause isomerization of the PIB backbone and produce, upon deactivation, various isomeric *tert*-chloride structures. In this way, normal *tert*-chloride end groups are depleted and replaced by multiple structures whose ^{1}H NMR chemical shifts are all unique but similar; thus, a number of new peaks are observed, all of which lie within the spectral region characteristic of protons positioned β to a chlorine atom. The theoretical possibility that carbenium ion rearrangements might serve as a psuedo-termination mechanism in carbocationic polymerization has been previously recognized.[15]

Figure 6 illustrates several of the many possible isomerization pathways, all beginning from the secondary carbenium ion, **2**, created when the ionized form of the normal PIB chain end (**1**) undergoes a 1,2-hydride shift. Although **2** is a secondary carbenium ion and is presumably less stable than **1**, it leads ultimately to more stable structures. For example, the normal PIB chain end comprises a carbocation which is bonded to two small (methyl) groups and one larger group; however, structure **3**, which results when **2** undergoes a 1,2-methide shift, consists of a carbocation which is bonded to only one methyl group and two larger groups. Increased back strain in the *tert*-chloride precursor facilitates carbocation formation and causes a larger ionization equilibrium constant; however, reactivity of the carbocation is decreased due to both energetic and steric factors. Structures **3** and/or **4** have been observed (as the olefin) both in commercial oligoisobutylene[16] and polybutene[17] (mixed C_4 olefin monomers) and in PIB prepared at high temperature (−20 °C).[16]

The isomerizations pictured in Figure 6 involve combinations of 1,2-hydride and 1,2-methide shifts only. It is quite possible that other types of reactions can occur. For example, it has been proposed in the literature that **1** can undergo a 1,3-methide shift.[18] This possibility was considered but rejected in light of the fact that Skell and Reichenbacher reported that the 3,3-dimethyl-1-butyl cation failed to form products that would have resulted from a 1,3-methide shift.[19] The loss of small hydrocarbon fragments by carbon−carbon bond cleavage[17,20] and the participation of intermolecular methide (or hydride) transfers are two possibilities that will be addressed in future work. The latter could be

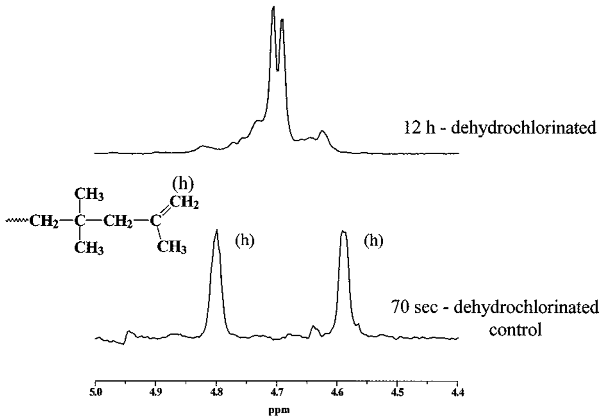

Figure 7. ^{1}H NMR spectra (olefinic region) of MeOH-quenched PIB after dehydrochlorination using potassium *tert*-butoxide: 70 s control and 12 h aged samples.

detected by rate measurements performed at several different overall polymer concentrations.

The proposed rearrangement mechanism is supported by the ATMS quenching results. The majority of the PIB chains remains active toward ATMS, evidenced by allyl functionalities which did not drop below 78%. However, the ^{1}H NMR resonances of the allyl groups were observed to change; in particular, the characteristic doublet, peak (f) in Figure 3, which represents the point of attachment of the allyl group to the PIB chain, disappeared. This process is similar to the disappearance of the normal *tert*-chloride functions; that is, a single dominant structure which is highly visible in the NMR spectrum is replaced by a number of minor isomeric structures, none of which are prominent. The failure of some chains to react with ATMS could be traced to steric or stability factors; some rearranged *tert*-chloride groups may be relatively inaccessible or, when ionized into carbenium ions, too stable.

To provide stronger support for this hypothesis, control and aged samples which were quenched with MeOH were dehydrochlorinated using potassium *tert*-butoxide. It was expected that the *exo*-olefin chain end, which is characteristic of dehydrochlorination of normal *tert*-chloride chain ends, would be replaced by multiple olefinic structures. Figure 7 shows ^{1}H NMR spectra (olefinic region) of the 70 s control and 12 h aged PIB, after dehydrochlorination. The control sample spectrum shows the characteristic peaks at 4.6 and 4.8 ppm due to the *exo*-olefin chain end. The aged sample spectrum is more complex, exhibiting a number of minor peaks and two dominant peaks, all within the spectral range of 4.5−4.9 ppm which is characteristic of vinylidene (asymmetric disubstituted) olefins. Integration, however, showed that the total area of the olefinic resonances was only 60−70% of the theoretical value calculated by assuming two olefinic protons per chain end. Two possible explanations present themselves. One is that the potassium *tert*-butoxide was unable to dehydrochlorinate all of the sites due to steric reasons. This will be investigated in future work by using, for example, a less hindered base or by performing quantitative thermal dehydrochlorination. The second possibility is the existence of significant amounts of either trisubstituted or tetrasubstituted olefin. The presence of trisubstituted olefin seems unlikely from the ^{1}H NMR data; the presence of tetrasubstituted olefin will be investigated in future studies using ^{13}C NMR.

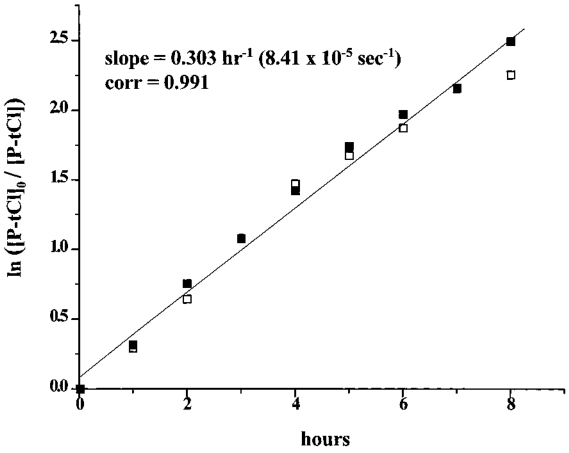

Figure 8. First-order depletion of *tert*-chloride end groups of PIB, measured by ^{1}H NMR integration of terminal dimethyl (solid squares) and methylene protons (hollow squares).

Kinetics of Rearrangement. The rate of *tert*-chloride end group depletion was measured via ^{1}H NMR (Figure 1), by integrating the area of either peak (a) or peak (c) relative to peak (b) for a number of different aging times up to 12 h. The data were treated using the kinetic scheme

$$\mathrm{P}{-}t\mathrm{Cl} \underset{k_{-1}}{\overset{k_1[\mathrm{TiCl_4}]^2}{\rightleftharpoons}} \mathrm{P^+C^-} \quad \text{fast} \tag{2}$$

$$\mathrm{P^+C^-} \xrightarrow{k_r} \mathrm{P_r} \tag{3}$$

where, P−*t*Cl is the *tert*-chloride chain end, $\mathrm{P^+C^-}$ is the active ion pair, and $\mathrm{P_r}$ is the rearranged chain end. It was assumed that the preequilibrium is fast relative to the second reaction and that the mass balance

$$[\mathrm{P}{-}t\mathrm{Cl}]_0 = [\mathrm{P}{-}t\mathrm{Cl}] + [\mathrm{P^+C^-}] + [\mathrm{P_r}] \tag{4}$$

holds, where, $[\mathrm{P}\text{-}t\mathrm{Cl}]_0$ is the total number of polymer chains, equal to the initiator concentration.

The rate of rearrangement was written as,

$$\text{rate} = \frac{\mathrm{d}[\mathrm{P_r}]}{\mathrm{d}t} = k_r[\mathrm{P^+C^-}] = \frac{k_r K}{1+K}([\mathrm{P}{-}t\mathrm{Cl}]_0 - [\mathrm{P_r}]) \tag{5}$$

where, $K = k_1[\mathrm{TiCl_4}]^2/k_{-1}$. Solution of differential eq 5 yields

$$[\mathrm{P_r}] = [\mathrm{P}{-}t\mathrm{Cl}]_0(1 - e^{-k_r K t/(1+K)}) \tag{6}$$

which transforms to

$$\ln\left(\frac{[\mathrm{P}{-}t\mathrm{Cl}]_0}{[\mathrm{P}{-}t\mathrm{Cl}]}\right) = k_r K t \tag{7}$$

when K is small, and thus $[\mathrm{P}{-}t\mathrm{Cl}]_0 \cong [\mathrm{P}{-}t\mathrm{Cl}] + [\mathrm{P_r}]$.

Figure 8 shows that the depletion of *tert*-chloride end groups does indeed follow first-order kinetics with an apparent rate constant for rearrangement, $k_{r\mathrm{app}} = k_r K$, of approximately 8×10^{-5} s^{-1}. Since the apparent rate constant for propagation, $k_{\mathrm{app}} = 5.3 \times 10^{-2}$ s^{-1}, was measured within the first minute or so of the reaction when rearrangement was still negligible, it is related to k_p as follows (for small K):

$$k_{app} = k_p[P^+C^-] = k_pK[P{-}tCl]_0 \qquad (8)$$

From these two apparent rate constants can be obtained the ratio

$$\frac{k_p}{k_r} = \frac{k_{app}}{k_{rapp}[P{-}tCl]_0} \qquad (9)$$

which, for this system under these conditions, assumes a value of 3×10^4 M^{-1}. Thus, the present system is a Class 4−5 living system according to Matyjaszewski.[2] As a final note, the possible participation of intermolecular hydride or methide transfer reactions, in addition to the proposed unimolecular isomerizations, would not be expected to alter the observed unit kinetic order since these external groups would be in sufficient excess that psuedo-first-order kinetics would be operative.

Conclusions

$TiCl_4$-based initiating systems are the preferred systems for controlled/living polymerization of high molecular weight PIB (for DP < 10^2, BCl_3-based systems are also used extensively). These results show that livingness of $TiCl_4$-based systems is limited not by chain transfer to monomer or unimolecular β-proton expulsion but rather by rearrangement or isomerization of the ionized chain ends to form species in which the active carbenium ion is no longer at the tip of the chain. The rearranged chain ends are thermodynamically more stable than the normal *tert*-chloride chain ends, and they are sterically hindered and less reactive; thus they may be viewed as psuedo-terminated. Obviously, rearrangement is occurring always during polymerization; but under normal circumstances it would be difficult to detect. Its rate constant is low relative to that for propagation, and thus it is not normally observed for systems in which the initiator concentration is high and the chain ends are readily observed by spectroscopy. At lower initiator concentration, rearrangement is more competitive with propagation, but chains that rearrange in the presence of a significant concentration of monomer can slowly reinitiate to regenerate the normal structure. In such a case, rearrangement could only be detected by the presence of a low concentration of short-chain branches along the PIB backbone. The conditions used herein, in which chain ends at relatively high concentration were aged for long periods in the virtual absence of monomer, are especially favorable toward detection of rearrangement.

The value of k_p/k_r allows the calculation of the fraction of chains that would be expected to have suffered rearrangement, at a given monomer converson, for example 98%, for various initiator concentrations, assuming that a rearranged chain is effectively terminated. For the system herein, with $[I]_0 = 2.3 \times 10^{-2}$ M, only 0.6% of the chains have rearranged by this point. If $[I]_0$ is decreased by a factor of 20, which, with $[IB]_0 = 1$ M, would yield M_n of about 50 000 for a monofunctional initiator, about 11% of the chains would have rearranged. These simple calculations show that rearrangement can begin to negatively impact controlled/living IB polymerization systems at rather moderate molecular weights. As a final note, it is expected that the k_p/k_t ratio will decrease with increasing temperature, raising the fraction of rearranged chains at a given conversion. This places a limitation on the utilization of living IB polymerization at higher temperatures.

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