β-Proton Elimination by Free Bases in the Living Carbocationic Polymerization of Isobutylene

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Introduction. Living cationic polymerizations today are based invariably on one of three approaches: (i) nucleophilic counterions, (ii) common ion salts, or (iii) nucleophiles ("Lewis bases" or "electron donors").[1,2] While the effects of common ion salts in the living cationic polymerization are more or less understood, those of nucleophiles are still under discussion.[3−7] Higashimura and Sawamoto proposed the theory of carbocationic stabilization by nucleophilic additives through weak nucleophilic interaction.[4,5] A similar opinion was also expressed by Kennedy et al.[1] In contrast to these views, according to Matyjaszewski, these bases may reversibly form inactive onium ions thereby controlling the rate of polymerization.[6] It has also been proposed by Penczek that, via onium ion formation, nucleophiles may also enhance the rate of equilibrium between dormant and active species and reduce polydispersities.[7] Nucleophiles may also affect the polymerization rate by coordination with the Lewis acid. The Lewis acid/nucleophile complex may still be strong enough to ionize the polymer halide ends of more reactive monomers; however, they are too weak to ionize dormant polymer ends of less reactive monomers. Finally, strong bases may also eliminate *β*-protons, which should be avoided.

Recently, we have demonstrated that the living cationic polymerization of vinyl monomers can be achieved using the proton trap 2,6-di-*tert*-butylpyridine (DTBP), which is a nonnucleophilic strong base.[8−10] Due to its inability to stabilize carbocations or to form complexes with Lewis acids (although propositions to the contrary have appeared[11,12]), it was concluded that the sole role of DTBP is to scavenge protic impurities in the polymerization system. Since the addition of nucleophilic additives such as dimethyl sulfoxide had no effect on polymerization rates, molecular weights, and their distributions when DTBP was also present, it was proposed that the main function of nucleophiles is to trap protic impurities.[9] Recent kinetic studies of the living polymerization of isobutylene (IB) in the presence of a series of amine-based nucleophilic additives by Storey et al. have also led to the same conclusion.[13]

While the use of DTBP as a proton trap in carbocationic macromolecular engineering has led us to the preparation of well-defined homopolymers of IB, vinyl ethers, and styrenic monomers and their block copolymers,[8−10,14−16] the possibility of the *β*-proton elimination by DTBP from living polyisobutylene (PIB) chain ends has been evoked in several reports.[17−20] Firmly convinced that DTBP cannot abstract a proton from the propagating PIB chain ends, we were startled when we actually detected substantial elimination when we changed a supplier of DTBP. These results have lent an impetus to the present study. A full report, which will be published elsewhere,[21] also includes 2-, and 2,6-alkyl-substituted pyridines to examine the scope and limitation of pyridine bases as proton traps in the living cationic polymerization of IB.

Experimental Section. The polymerizations were carried out using the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$/IB/hexane (Hex):methyl chloride (MeCl) (60:40, v:v)/−80 °C system in the presence of DTBP with 99% purity by GC (Aldrich) or 94% purity by GC (Maybridge Chemical Co., Trevillet, U.K.), and the latter will be referred to as DTBP-94 for comparison. Using this system, the polymerization reached 50% conversion in 8 min and the complete conversion was obtained in 1 h. Low M_ns were planned to help identify the chain-end structure, and low initiator concentration (2×10^{-3} M) was used to avoid or minimize coupling. End-group analysis was carried out using ^{1}H NMR spectroscopy (250 MHz, $CDCl_3$) and relative amounts of the *exo*-olefin were calculated by comparing the integration areas of two vinyl protons ($\delta = 4.62-4.85$ ppm) with those of terminal methyl ($\delta = 1.67$ ppm) or methylene protons ($\delta = 1.95$ ppm) adjacent to chloro ends. Low-temperature ^{1}H NMR experiments were performed on a Bruker 250 MHz spectrometer equipped with a variable-temperature controller which regulates the temperature to ±0.5 °C. CD_2Cl_2 was refluxed over CaH_2 overnight and distilled prior to the sample preparation. Samples were prepared in a glovebox and sealed under nitrogen atmosphere. More detailed experimental conditions will be published elsewhere.[21]

Results and Discussion. End-group analysis by ^{1}H NMR spectroscopy carried out with low M_n PIBs revealed that PIBs, obtained using DTBP-94 and quenched with methanol after 1 h (∼100% conversion), invariably carry ∼20% *exo*-olefin and ∼80% chloro ends. In contrast, negligible amounts of elimination were observed when DTBP was used. Interestingly, in parallel experiments using DTBP and DTBP-94, polymerization rates, M_ns, and molecular weight distributions were nearly identical. To determine whether this elimination occurred during polymerization or during workup, in subsequent experiments samples were taken at 15 min, after 1 h, and after 3 h. Independently, the incremental monomer addition (IMA) technique was also employed after ∼100% IB conversion. With DTBP, negligible amounts of elimination were observed by ^{1}H NMR even after 3 h, and PIB obtained in IMA experiment exhibited, as can be seen in Figure 1A, a clean shift of GPC trace to doubled molecular weight indicating the absence of termination before IMA.

However, with DTBP-94, the extent of elimination increased with time (∼6% in 15 min, ∼20% in 1 h, and ∼40% in 3 h), and this elimination was conspicuously observed from the GPC traces, as can be seen in Figure 1B. PIB obtained after 3 h exhibits a small hump at lower elution volume, which is attributed to the coupled product as a result of the *exo*-olefin formation. A small tail at higher elution volume of the sample obtained by IMA also indicates the possibility of termination before the addition of a second monomer charge. Two important findings should be noted from these results. First and most importantly, DTBP is truly inert toward the carbocationic active centers, as confirmed by ^{1}H NMR and GPC analyses; consequently impurities in DTBP-94 are responsible for the elimination. Second, the proton abstraction with DTBP-94 occurs *during* the polymerization (i.e., in the presence of monomer) as well as under monomer starved conditions.

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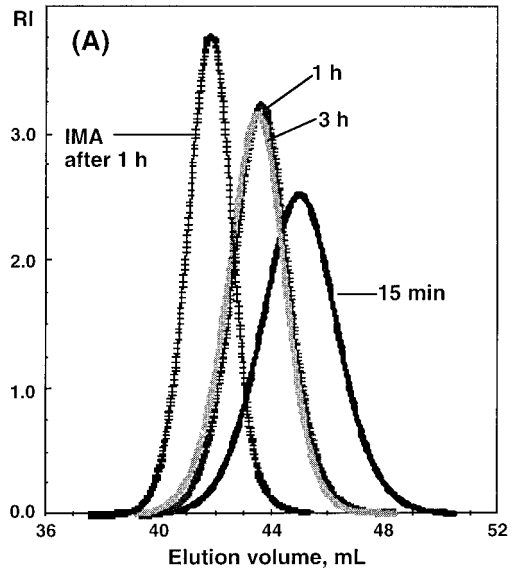

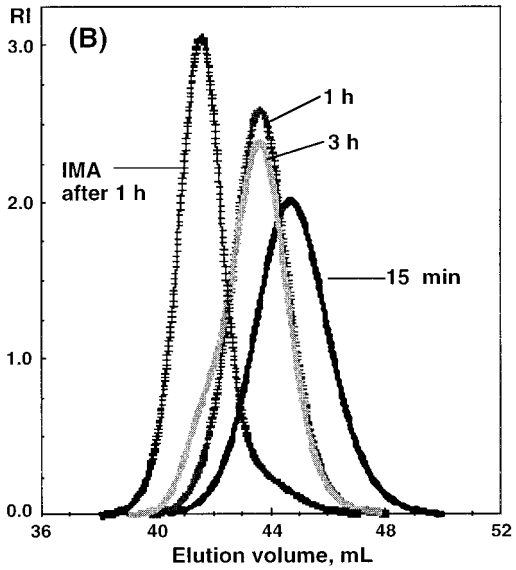

Figure 1. GPC traces of PIBs prepared using DTBP (A) or DTBP-94 (B) as a proton trap. Polymerization conditions: [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [proton trap] = 0.003 M, and [IB] = 0.072 M in Hex/MeCl (60/40, v/v) at −80 °C. $10^{-3}M_n$ and M_w/M_n (polymerization time): (A) 1.3 and 1.20 (15 min); 2.0 and 1.18 (1 h); 3.9 and 1.17 (2 h by IMA); 2.1 and 1.19 (3 h), (B) 1.2 and 1.20 (15 min); 2.1 and 1.18 (1 h); 4.0 and 1.24 (2 h by IMA); 2.0 and 1.28 (3 h).

Vigorous purifications of DTBP-94 by (i) column chromatography followed by distillation from CaH_2, (ii) recrystallization at low temperature followed by distillation from CaH_2, and (iii) fractional distillation from CaH_2 using a Nester-Faust spinning band apparatus were all successfully used to remove impurities responsible for the elimination, which was proved in subsequent polymerization experiments. GC-MS of purified and unpurified DTBP-94 identified traces of a sterically hindered *cyclic imine base* present in 0.2% (!) as the culprit. Therefore, we postulated that this nucleophile is sterically too hindered to quantitatively yield complex with $TiCl_4$, but its approach to the carbocations is not completely prevented. It is important to note that a compound present at $\sim 6 \times 10^{-6}$ M concentration cannot bind $\sim 10^{-3}$ M protons, and therefore, we have to presume proton transfer to DTBP via nitrogen to nitrogen proton trasfer.[22,23]

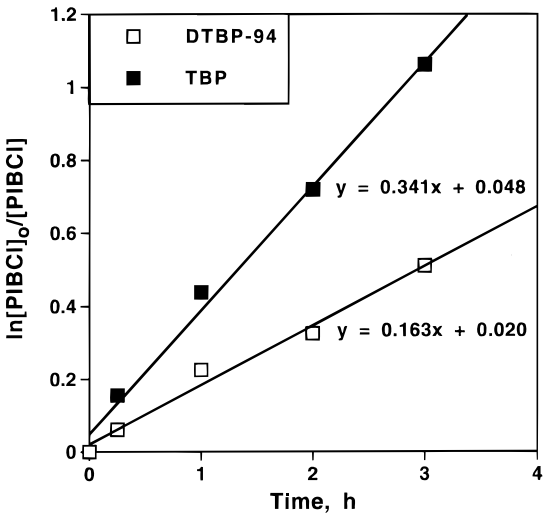

Figure 2. First-order plots of proton elimination in the presence of TBP and DTBP-94. Experimental conditions are listed in Figure 1.

Incited by this interpretation, we extended our study of the elimination reaction as a function of time in the presence of 2-*tert*-butylpyridine (TBP), which may closely model a free base in DTBP-94. In line with our hypothesis, extensive elimination was observed as a function of time, yielding exclusively the *exo*-olefin, under the same conditions as with DTBP-94. Interestingly, the elimination by free bases exhibited pseudo-first-order kinetics with respect to the carbocationic active species as shown in Figure 2.

Since [PIBCl] ≫ [$PIB^+Ti_2Cl_9^-$], the rate of elimination can be expressed in terms of the rate of PIBCl disappearance

$$d[PIBCl]/dt = -k[PIB^+Ti_2Cl_9^-][B] \qquad (1)$$

where B represents a free strong base. Considering the equilibrium between active and dormant species and its equilibrium constant (K), eq 1 can be rewritten as

$$d[PIBCl]/dt = -kK[PIBCl][TiCl_4]^2[B] \qquad (2)$$

Assuming [$TiCl_4$] and [B] as constants, integration of eq 2 yields a semilogarithmic kinetic equation as shown in eq 3. In the case of DTBP-94, the assumption that

$$\ln([PIBCl]_o/[PIBCl]) = kK[TiCl_4]^2[B]t \qquad (3)$$

[B] is constant is supported by the fact that DTBP is a stronger base than any other pyridine derivatives in gas phase, and proton transfer from alkyl-substituted pyridines to DTBP is a diffusion-controlled process.[23−25]

In the case of TBP, however, the concentration of free TBP inevitably decreases with increased elimination and the observed linearity might be associated with the coupling reaction of olefinic PIB. When the extent of elimination was above 20%, the coupling reaction of olefinic PIB with the living chain end was significantly observed from both ^1H NMR and GPC analyses. Since this coupled carbocationic species is expected to have a higher ionization equilibrium constant due to the presence of *back strain*, i.e., the release of steric strain during rehybridization from sp^3 to sp^2, the rate of proton abstraction for this species may be much faster compared to that for its precursor.[26]

Table 1. Degree of Complexation and Equilibrium Constants at Various Temperatures[a]

temp, °C	$\alpha = ([TBP{\cdot}TiCl_4]/[TBP]_o)$	K_{com}, l/mol
25	0.33	1.86×10^1
10	0.51	4.12×10^1
0	0.67	8.71×10^1
−20	0.95	1.00×10^3

[a] $[TBP]_o = 0.01$ M and $[TiCl_4]_o = 0.03$ M in CD_2Cl_2.

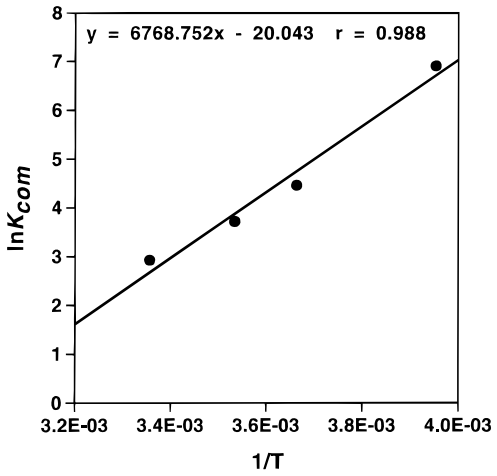

Figure 3. Arrhenius plot for the complexation of TBP with $TiCl_4$ in CD_2Cl_2.

Assuming 1:1 complex formation between TBP and $TiCl_4$, the equilibrium constant, K_{com}, can be calculated in terms of the degree of complexation, α (=$[TBP{\cdot}TiCl_4]/[TBP]_o$), and the initial concentrations of TBP and $TiCl_4$.

$$K_{com} = \frac{\alpha}{(1-\alpha)([TiCl_4]_o - \alpha[TBP]_o)} \qquad (4)$$

The degree of complexation, α, was calculated from the chemical shifts of aromatic protons of free (δ_{free}) and complexed TBP (δ_{com}) using ^1H NMR spectroscopy. The fast exchange of $TiCl_4$ was evidenced by the coalesced resonance peaks for both species and these peaks were fairly sharp over the wide range of temperature (−80 to +37 °C). Since the amount of protonated TBP was negligible, only two species, i.e., free and complexed TBP, were taken into consideration. α was calculated according to the equation $\alpha = \Delta\delta/\Delta\delta_{max}$ where $\Delta\delta = \delta_{sample} - \delta_{free}$ and $\Delta\delta_{max} = \delta_{com} - \delta_{free}$. δ_{com} was obtained by decreasing temperature and by increasing the concentration of $TiCl_4$ until there was no further downfield shift. A summary of the results is given in Table 1. These equilibrium constants at each temperature were plotted vs reciprocal temperature as shown in Figure 3. A straight line was obtained with a high correlation coefficient. The slope of this line is proportional to the heat of complexation, which was calculated to be about -13.5 kcal mol^{-1} K^{-1} in CD_2Cl_2. By extrapolation, the concentration of free TBP was calculated to be 2.8×10^{-8} M in CD_2Cl_2 at −80 °C. Assuming that solvent polarity has little effect on K_{com}, this level of free TBP is present in the polymerization system.

Conclusions. The major implication of these results is that, in order for nucleophilic additives to be used as proton traps in living cationic polymerization, they should quantitatively complex with Lewis acids; otherwise, their approach to the carbocationic active species should be completely blocked as with DTBP. Furthermore, the highest purity should be ensured and it must be confirmed that the impurities themselves do not cause elimination. Since the observed elimination is the result of an uncomplexed base in extremely low concentration, DTBP should be used in concentrations only slightly higher than the concentrations of protic impurities (typically $(1-2) \times 10^{-3}$ M). Using high concentrations does not have any advantage. On the contrary, it may result in proton elimination due to the increased concentration of basic impurities,[20] for which complex formation with $TiCl_4$ is hindered by steric compression, but approach of the polymer cation is not fully blocked.

Another important conclusion of the present study is that, at least in the polymerization of IB, the concept of carbocation stabilization or onium ion formation by a free nucleophile must be ruled out. Although it remains to be confirmed, it seems likely that this conclusion is generally applicable to other hydrocarbon olefins.

While β-proton elimination should be avoided for the synthesis of well-defined macromolecules, if diffusion control of this process can be shown, it may provide a novel method of establishing the concentrations of active centers, from which absolute propagation rate constants could be calculated. Research along this line is in progress.

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