THE ROLE OF PYRIDINE DERIVATIVES IN LIVING CARBOCATIONIC POLYMERIZATION: LEWIS BASE OR NUCLEOPHILE ?

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Abstract: The living cationic polymerization of isobutylene induced by the 2-chloro-2,4,4-trimethylpentane/$TiCl_4$/hexane:methyl chloride (60:40, v:v)/-80°C system was studied in the presence of pyridine derivatives. Protic initiation, substantial in the absence of these additives, was virtually eliminated in their presence, and polyisobutylenes with controlled molecular weight and narrow molecular weight distribution were obtained. With some additives, however, proton elimination occurs, resulting in the exclusive formation of the exo olefin. The rate of elimination is independent of monomer concentration, i.e., it occurs during and after the polymerization. Results suggest that the proton elimination is due to the presence of an uncomplexed base, especially when complex formation with $TiCl_4$ is hindered by steric compression, but its approach of the polymer cation is not fully blocked.

INTRODUCTION

Some of the pronounced advances in the living cationic polymerization of vinyl monomers has been seen in the beneficial applications of nucleophilic additives, which were reported to suppress chain breaking reactions such as termination and chain transfer.[1,2] These additives have already been used in the conventional cationic polymerization of vinyl monomers as earlier as the 1940s, and reported to inhibit or retard the cationic polymerization of styrene or isobutylene.[3] George et al. interpreted this inhibition or retardation in terms of "carbocation stabilization by the formation of onium ions".[3] The role of nucleophiles (Lewis base or electron donor) in contemporary living cationic polymerizations is still under discussion.[4-8] Higashimura and Sawamoto proposed the theory of carbocation stabilization by nucleophilic additives through weak nucleophilic interaction.[5,6] 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.[7] It has also been proposed by Penczek that, via onium ion formation, nucleophiles may enhance the rate of equilibrium between dormant and active species resulting

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in reduced polydispersities.[8] Nucleophiles may also affect the polymerization rate by coordination with Lewis acids. 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 is detrimental to the control of polymerization.

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 non-nucleophilic strong base.[9-11] Due to its inability to stabilize carbocations or to form complexes with Lewis acids (although propositions to the contrary have appeared[12,13]), 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.[10] 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.[14]

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,[9-11,15-17] the possibility of the β-proton elimination by DTBP from living polyisobutylene (PIB) chain ends has been evoked in several reports.[18-21] 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 the supplier of DTBP. Further investigations revealed that the proton elimination is due to the presence of an uncomplexed base. These results have lent an impetus to the present study. We have also included 2-, and 2,6-alkyl substituted pyridines in this study to examine the scope and limitation of pyridine bases as proton traps in the living cationic polymerization of IB.

EXPERIMENTAL

Pyridine (Py) was dried by refluxing with solid potassium hydroxide, followed by fractional distillation. 2-Ethylpyridine (EtP), 2,6-dimethylpyridine (DMP), and 2-*tert*-butylpyridine (TBP) was used as received from Aldrich. DTBP with 99% purity by GC (Aldrich) or 94% purity by GC (Maybridge Chemical Co., UK) was used as received and the latter will be referred to as DTBP-94 for comparison. All other chemicals and solvents were purified as described previously[9-11] or used as received.

Polymerization was carried out in a 75 mL test tube under a dry ($[H_2O] < 1.0$ ppm) nitrogen atmosphere in an MBraun 150-M glovebox (Innovative Technology Inc.). PIBs with low molecular weight ($M_n \sim 2{,}000$ g/mol) were prepared to help identify the chain-end structures by the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$/-80 °C system using

hexane (Hex)/methyl chloride (MeCl) solvent mixture (60/40, v/v) in the presence of a proton trap. In addition, low initiator concentration (0.002 M) was used to avoid or minimize the possible coupling reaction through olefinic PIB. Purification procedure of the product has already been reported.[9-11]

Molecular weights were measured using a Waters HPLC system equipped with Model 510 HPLC pump, Model 486 tunable UV/Vis detector, Model 712 sample processor, five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5 and 100 Å (Waters), Model 250 dual detector (refractometer/viscometer, Viscotek), and on-line multiangle laser light scattering (MALLS) detector (DAWN DSP-F, Wyatt Technology Inc.). 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.

RESULTS AND DISCUSSION

1. β-Proton Elimination by Free Bases

End-group analysis by ^{1}H NMR spectroscopy carried out with low M_n PIBs revealed that PIBs, obtained using DTBP-94 (94% by GC) and quenched with methanol after 1 h (~100% conversion), invariably carry ~20% exo-olefin and ~80% chloro ends. In contrast, negligible amounts (0 ~ 3%) 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 (MWDs) 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, 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 1(A), 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 1(B). PIB obtained after 3 h exhibits a small hump at lower elution volume, which is attributed to the coupled product as a result of 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. A summary of GPC analysis is given in Table 1. While broadening in MWDs of PIBs prepared in the presence of DTBP-94 was observed with increased extent of elimination, interestingly other polymerization characteristics such as conversion and M_n exhibited no discernible differences compared to those of PIBs prepared in the presence of DTBP.

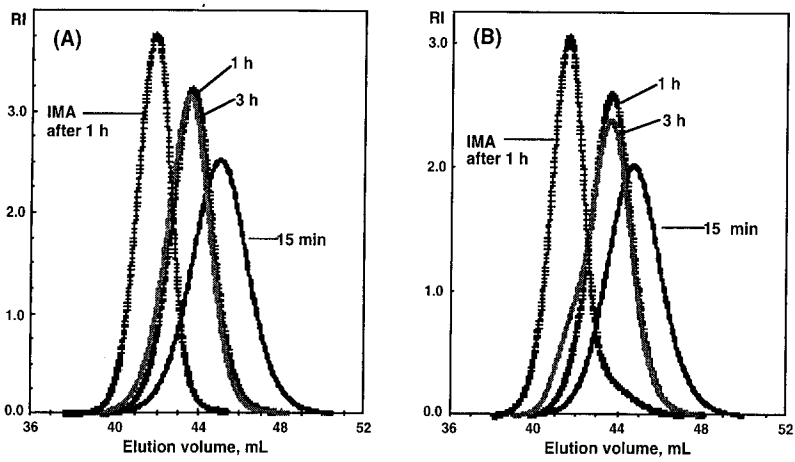

Figure 1. GPC traces of PIBs prepared using DTBP (A) and DTBP-94 (B) as a proton trap. Polymerization conditions: [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [proton trap] = 0.003 M, and [IB] = 0.072 M in Hex/MeCl (60/40, v/v) at -80°C.

Table 1. GPC Results of PIBs Prepared in the Presence of DTBP and DTBP-94

Polymerization time	DTBP		DTBP-94	
	10^{-3} x M_n	M_w/M_n	10^{-3} x M_n	M_w/M_n
15 min	1.3	1.20	1.2	1.20
1 h	2.0	1.18	2.1	1.18
2 h[a]	3.9	1.17	4.0	1.24
3 h	2.1	1.19	2.0	1.28

[a] IMA after ~100% IB conversion (1h).

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 ^1H NMR and GPC analyses; consequently impurities in DTBP-94 are responsible for the elimination. Secondly, the proton abstraction with DTBP-94 occurs *during* the polymerization (i.e., in the presence of monomer) as well as under monomer starved conditions. This indicates that the rate of elimination is considerably high and this process might be competitive with propagation.

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

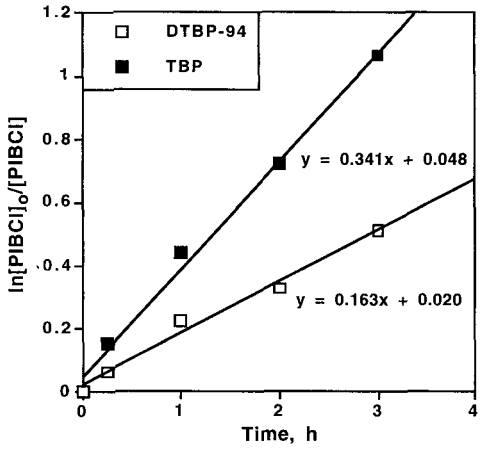

Figure 2. First-order plots of proton elimination in the presence of TBP and DTBP-94. Experimental conditions are listed in Figure 1.

culprit. Therefore, we postulated that this nucleophile is sterically too hindered to quantitatively yield complexes with $TiCl_4$, but its approach of the carbocations is not completely prevented. It is important to note that a compound present at ~$6x10^{-6}$ M concentration cannot bind ~10^{-3} M protons, and therefore, we have to presume proton transfer to DTBP via nitrogen to nitrogen proton transfer [22,23].

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 the 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, this 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 (d([PIBCl] + [$PIB^+Ti_2Cl_9^-$]) /dt)can be expressed in terms of the rate of PIBCl disappearance:

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

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:

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

Assuming [$TiCl_4$] and [B] as constants, integration of Eq 2 yields a semilogarithmic kinetic equation as shown in Eq 3.

$$\ln([PIBCl]_0/[PIBCl]) = kK[TiCl_4]^2[B]t \quad (3)$$

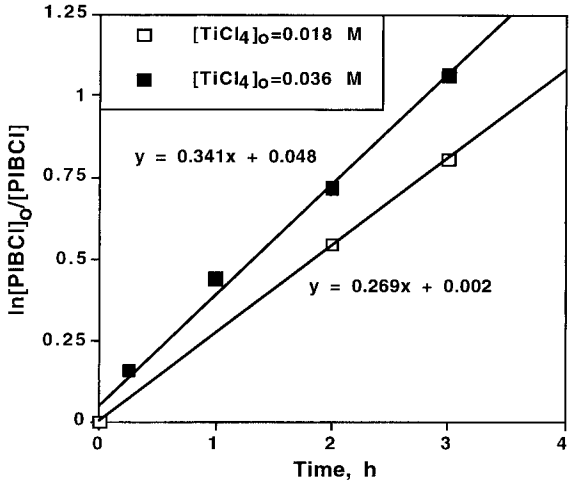

Figure 3. Proton elimination at different $[TiCl_4]_0$ using TBP as a proton trap.

Corollary to the assumption that [B] is constant is 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 other words, the observation of pseudo-first-order kinetics is easily explained in the case of DTBP-94, where proton abstraction is carried out by a constant and catalytic amount of a cyclic imine base, and the protons are rapidly transferred to an excess of DTBP. 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 the olefinic PIB. When the extent of elimination was above 20%, the coupling reaction of olefinic PIB with the living chain end was 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 may be much faster compared to its precursor.[26] In order to collect further information, elimination rates were measured by increasing or decreasing the concentration of $TiCl_4$ ($[TiCl_4]_0$ = 0.072 or 0.018 M). Using $[TiCl_4]_0$ = 0.072 M, the calculation was complicated due to significant amounts of the coupled product especially at higher extent of elimination. Results using $[TiCl_4]_0$ = 0.018 and 0.036 M are compared in Figure 3, and it appears that free TBP, which is in a fast equilibrium with complexed TBP, is responsible for the observed proton elimination.

Assuming 1:1 complex formation between TBP and $TiCl_4$ and using stoichiometry ($[TBP]_0$=[TBP]+[TBP·$TiCl_4$] and $[TiCl_4]_0$= [$TiCl_4$]+[TBP·$TiCl_4$]), the equilibrium constant,

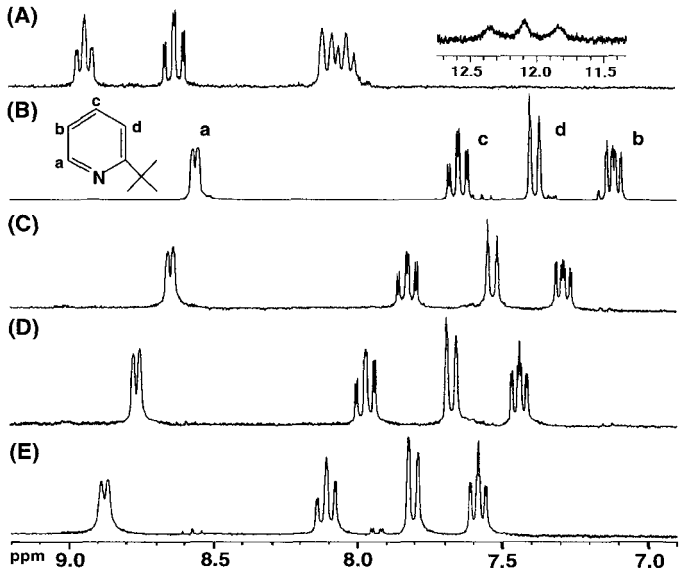

Figure 4. Expanded 250 MHz ^1H NMR spectra (CD_2Cl_2) of protonated TBP (A), free TBP (B), complexed TBP with $TiCl_4$ at 25 °C (C), 0 °C (D), and -30 °C (E).

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 100% 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 a wide range of temperature (-80 °C to 37 °C). Figure 4 shows ^1H NMR spectra of aromatic protons of protonated TBP (A), free TBP (B), and complexed TBP with $TiCl_4$ (C-E). ^1H NMR spectrum of protonated TBP (A) was easily obtained when a normal sampling procedure was followed without drying the solvent (CD_2Cl_2). Quantitative protonation of TBP complex was confirmed from the integration ratio of aromatic protons (δ = 7.9 ~ 9.1 ppm)/the N-H proton (δ = 11.7 ~ 12.5 ppm) which was four. Since the amount of protonated TBP in the TBP complex was negligible as can be seen from Figure 4 (C-E), only two species, i.e., free and complexed TBP were taken into consideration. Using the average chemical shifts of aromatic protons, α was calculated according to the equation $\alpha = \Delta\delta/\Delta\delta_{max}$ where $\Delta\delta = \delta_{sample} - \delta_{free}$ and $\Delta\delta_{max} = \delta_{com} - \delta_{free}$. And δ_{com} was obtained by decreasing

Table 2. Degree of Complexation and Equilibrium Constant at Various Temperature[a]

Temperature, °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.

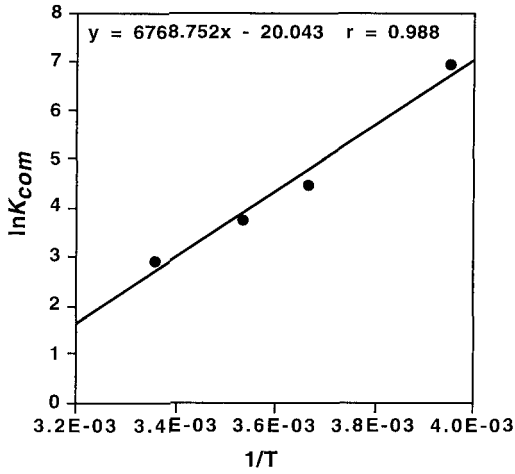

Figure 5. Arrhenius plot for the complexation of TBP with $TiCl_4$ in CD_2Cl_2.

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 2. These equilibrium constants at each temperature were plotted versus reciprocal temperature as shown in Figure 5. 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. Even though direct extrapolation of this equilibrium constants to polymerization system is not available due to different solvent polarity, from the Arrhenius plot in Figure 4, the concentration of free TBP is calculated to be ~2.8×10^{-8} M at -80 °C, provided that solvent effect is negligible.

2. Pyridine Derivatives as Proton Traps

Pyridine derivatives such as pyridine or 2,4-dimethylpyridine have extensively been used in the living cationic polymerization of IB by others.[14,27] While their role is still disputed, it is indubitable that in their presence protic initiation is prevented, i.e., they are proton traps. In sharp contrast to the results with TBP, these less hindered pyridine bases

Table 3. GPC Results of PIBs Prepared in the Absence and Presence of Pyridine Derivatives.

Pzn	no proton trap		Py		EtP		DMP	
time	$10^{-3}xM_n$	M_w/M_n	$10^{-3}xM_n$	M_w/M_n	$10^{-3}xM_n$	M_w/M_n	$10^{-3}xM_n$	M_w/M_n
15 min	2.4	5.93	1.5	1.68	1.7	1.17	1.7	1.19
1 h	2.8	5.28	2.5	1.28	2.6	1.17	2.7	1.14
2 h[a]	4.8	3.34	4.7	1.16	5.9	1.14	5.0	1.14
3 h	2.6	4.13	2.5	1.16	2.7	1.14	2.6	1.13

[a] IMA after ~100% IB conversion (1h).

reportedly induce the living polymerization of IB. Therefore, the question remained as to the scope and limitation of pyridine bases as proton traps in the living cationic polymerization of IB. We extended our study to other pyridine bases such as pyridine (Py), 2-ethylpyridine (EtP), and 2,6-dimethylpyridine (DMP) to examine the possible elimination by free uncomplexed species as well as their proton scavenging abilities. The same experimental protocol was employed as with DTBP, DTBP-94, and TBP. For comparison, IB polymerization was also carried out in the absence of these proton traps and otherwise under same conditions. Figure 6 shows the GPC traces of the products in the absence of a proton trap (A), and in the presence of Py (B), EtP (C), or DMP (D), and the results were summarized in Table 3.

In the absence of these additives, GPC traces of the products exhibited bimodal or multimodal distributions with the peak at lower elution volume (M_p = 35,000) attributed to protic initiation. However, in the presence of these additives, IMA experiments exhibited clean shifts of GPC traces to almost doubled M_ns after ~100% monomer conversion, and no evidence was obtained from ^1H NMR spectroscopy for the proton elimination even after 3 h of polymerization time. Interestingly, in the case of EtP, no precipitate was formed throughout the polymerization indicating that both EtP complex with $TiCl_4$ and its protonated counterpart is completely soluble at a given condition. As reported, copious yellow precipitates were formed in the case of Py and small amounts of white precipitates deposited in the bottom of the reactor in the case of DMP.

GPC results along with ^1H NMR spectroscopy lead us to the conclusion that these pyridine derivatives quantitatively form complex with $TiCl_4$ and they can be used as proton traps at least at a given condition. However, a question also arises concerning the relative strength of proton scavenging by these pyridine derivatives. Indirect comparison of proton scavenging strength between DTBP and Py was made from the extent of hydrochlorination of PIB-olefin by protic impurities. For this purpose, PIB-Cl with low M_n (= 980 g/mol) was prepared and this was converted to PIB-olefin according to the procedure reported by Kennedy et al..[28] This PIB-olefin was mixed with a solvent mixture (Hex/MeCl 60/40, v/v), $TiCl_4$ and DTBP or Py at similar conditions to those employed in the polymerization.

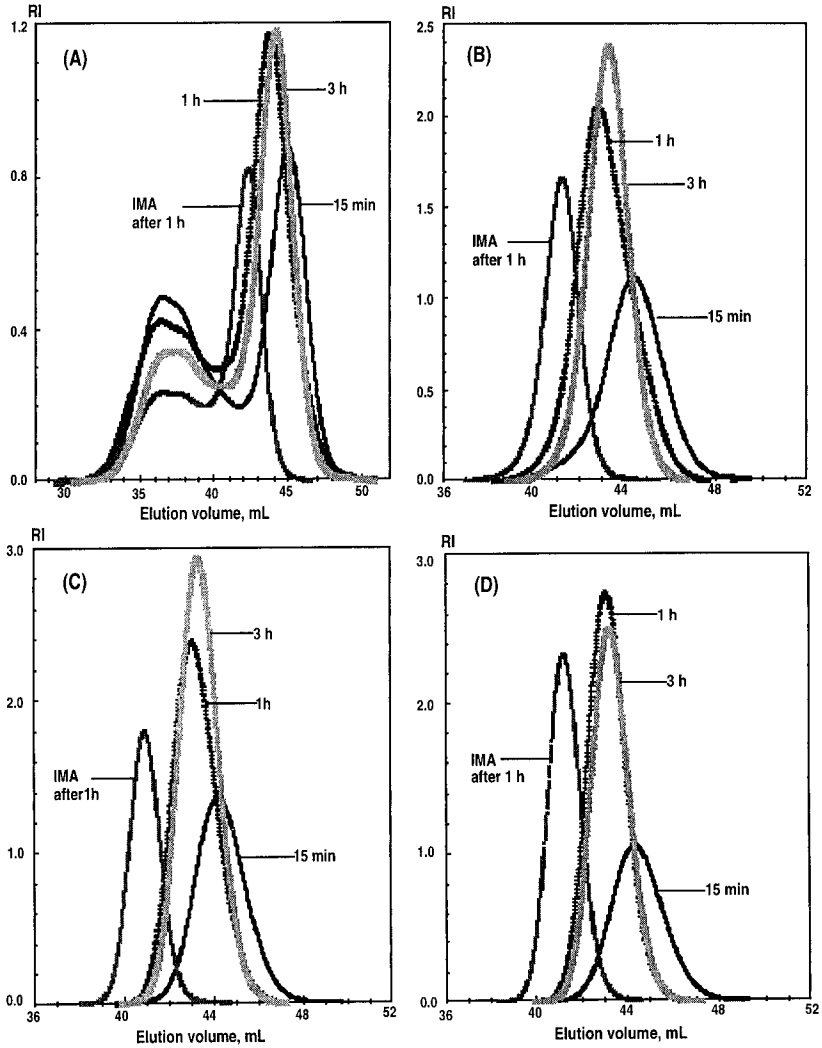

Figure 6. GPC traces of PIBs prepared in the absence of a proton trap (A), and in the presence of Py (B), EtP (C), or DMP (D). Polymerization conditions: [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [proton trap] = 0.003 M, and [IB] = 0.077 M in Hex/MeCl (60/40, v/v) at -80°C.

Table 4. Extent of Hydrochlorination in the Presence of DTBP or Py[a]

sample no.	proton trap	PIB-olefin, %	PIBCl, %
1	DTBP	~100	~0
2		~100	~0
3	Py	90	10
4		90.6	9.4

[a]Reaction conditions: [PIB-olefin] = 0.003 M, [$TiCl_4$] = 0.036 M, and [proton trap] = 0.003 M, in Hex/MeCl (60/40, v/v), at -80 °C.

After 5 min, $TiCl_4$ was deactivated by the addition of methanol. The extent of hydrochlorination by protic impurities should be inversely proportional to the strength of proton traps, and can be determined by ^1H NMR structural analysis of the recovered products. A summary of the results is given in Table 4. It is notable that ~10% of hydrochorination of PIB-olefin was observed when Py was used as a proton trap. Since HCl is also expected to evolve during quenching with methanol where titanium chloride is converted to titanium methoxides, it was not clear whether this hydrochlorination is due purely to protic impurities or to HCl produced during quenching with methanol.

In order to answer this question, a large excess of Py, instead of methanol, was used as a quenching agent in the subsequent experiment. Since a large excess of Py deactivates $TiCl_4$ by the formation of a strong complex which is stable even after quenching with methanol, using Py as a quenching agent can distinguish hydrochlorination by protic impurities from that during a quenching process. After 5 min of the addition of PIB-olefin which was a last entry, $TiCl_4$ was deactivated by the addition of Py or Py solution. As can be seen in Table 5, characterization results by ^1H NMR spectroscopy of recovered products were similar to those given in Table 4.

Table 5. Extent of Hydrochlorination Using Py as a Quenching Agent[a]

sample no.	proton trap	PIB-olefin, %	PIBCl, %	quenching agent
1	DTBP	~100	~0	2 mL Py
2		~100	~0	5 mL Py sol'n[b]
3	Py	91.1	8.9	2 mL Py
4		94.6	6.4	5 mL Py sol'n[b]

[a]Reaction conditions: [PIB-olefin] = 0.003 M, [$TiCl_4$] = 0.036 M, and [proton trap] = 0.003 M, in Hex/MeCl (60/40, v/v), at -80 °C. [b]5 M solution in Hex.

These results verify that the observed hydrochlorination is due largely to protic impurities and it is also concluded that Py is a relatively weak proton trap at a given condition. While this might be attributed to the relative insolubility of Py complex in the polymerization medium, this clearly indicates that DTBP is a superior proton trap to Py in the living cationic polymerization of IB.

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 $1\text{-}2\text{x}10^{-3}$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 their 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.

Prydine derivatives such as Py, EtP, and DMP exhibited significant proton scavenging capabilities at a given condition and it is concluded that they quantitatively form complex with $TiCl_4$. Based on hydrochlorination experiments of PIB-olefin, it is also concluded that DTBP is a superior proton trap to Py.

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