Investigation of the effect of epoxide structure on the initiation efficiency in isobutylene polymerizations initiated by epoxide/TiCl₄ systems

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Abstract

The effect of the chemical structure of styrene-based epoxides, namely, styrene epoxide (SE), α-methylstyrene epoxide (MSE), *p*-methylstyrene epoxide (pM-SE) and α-methyl-*p*-methylstyrene epoxide (pM-MSE), in conjunction with TiCl₄, on the initiation efficiency (I_{eff}) in the carbocationic polymerization of isobutylene (IB) was investigated. SE yielded living polymerization, but the initiation efficiency was low when compared to MSE (I_{eff} = 8% and 35%, respectively). pM-SE led to non-living IB polymerization, while pM-MSE revealed linear M_n-conversion plot and narrow MWD with a non-linear first order rate plot. Among the epoxides investigated, MSE was the best initiator to scale up the one-step synthesis of polyisobutylenes (PIBs) carrying one *primary* hydroxyl head group and one *tertiary* chloride end group. The hydroxyl functionality of these PIBs determined by ¹H-NMR was $F_n = 1.09 \pm 0.16$ from 24 experiments.
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1. Introduction

We reported, for the first time, that substituted epoxides such as α-methylstyrene epoxide (MSE), 2,4,4-trimethyl-pentyl-epoxide-1,2 (TMPO-1), 2,4,4-trimethyl-pentyl-epoxide-2,3 (TMPO-2) and hexaepoxi squalene (HES), shown in Scheme 1, were able to initiate the carbocationic polymerization of isobutylene (IB) in conjunction with titanium tetrachloride (TiCl₄) [1–3].

Linear polymers were obtained from MSE, TMPO-1 and TMPO-2, whereas HES yielded star-branched polymers. The initiator efficiencies ($I_{eff} = M_n/M_{n,theo}$ where M_n and $M_{n,theo}$ is the measured and theoretically expected number-average molecular weight) were 35%

for MSE and 40% for HES, while TMPO-1 and TMPO-2 yielded low I_{eff} values of 3% and 10%, respectively. A competitive reaction mechanism was proposed for the initiation [1], according to which I_{eff} was determined by the competition between S_N1 and S_N2 mechanistic pathways, as shown in Scheme 2. The carbenium ions forming in the S_N1 pathway initiated the carbocationic polymerization of IB, while the initiator reacting in the S_N2 pathway was "lost" in terms of carbocationic activity.

Structural characterization of the polymer resulting from the MSE/TiCl₄ initiating system by NMR and IR spectroscopic analysis later confirmed the presence of a *tertiary* chloride end group [1] and a *primary* hydroxyl head group [4].
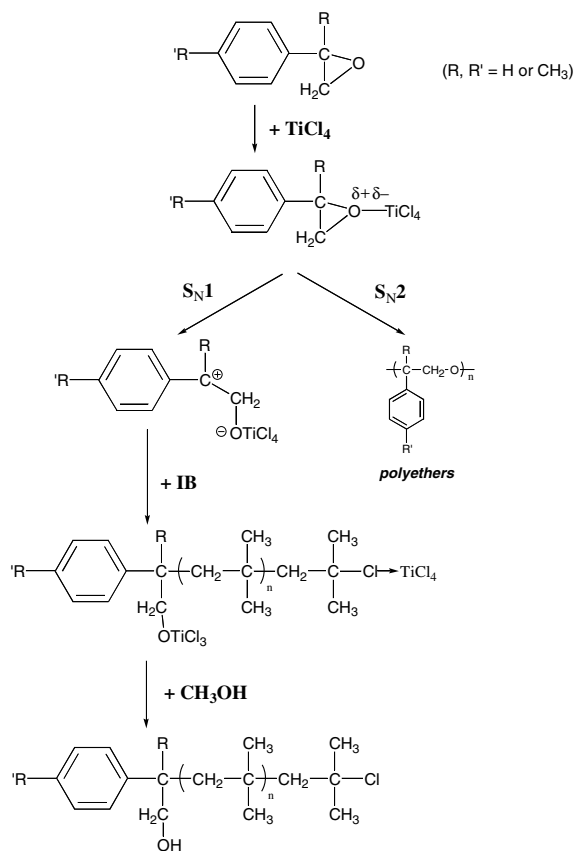
Epoxides are commercially available and can be synthesized easily by relatively simple synthetic methods [1,5]. They are therefore widely used as monomers for polyether synthesis by both cationic and anionic

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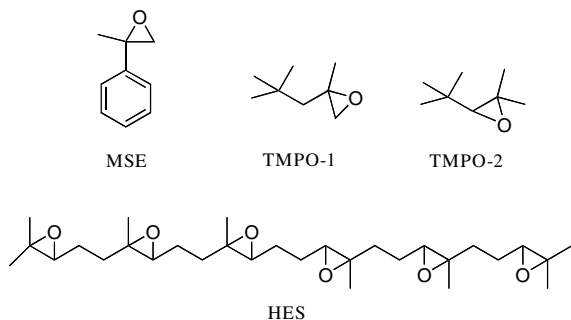
Scheme 1. Epoxide initiators.

Scheme 2. Proposed initiating mechanism for the MSE/TiCl$_4$/IB system [1].

polymerizations. In comparison with anionic polymerization, the degree of polymerization obtained from cationic polymerization is low [6,7]. For instance, polyethers obtained by the cationic polymerization of MSE initiated by trityl-(hexachloro antimonite) had low number-average molecular weight (M_n), ranging from 500 to 1000 g/mol, with low yield [8,9]. Interestingly, substituted epoxides in conjunction with Lewis acids were originally found to be inactive in initiating cationic polymerization.
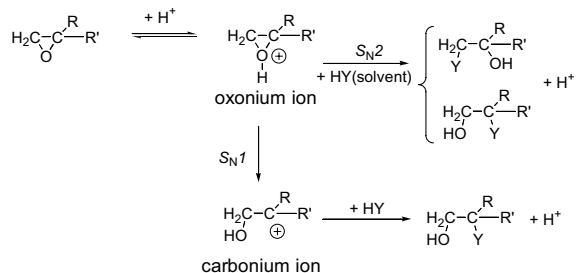

Scheme 3. Suggested ring-opening mechanism in the acidic cleavage of epoxides [6].

Dreyfuss and Kennedy attempted to initiate the polymerization of tetrahydrofuran (THF) by 2,4,4-trimethyl-pentyl-epoxide-2,3/BF$_3$, unsuccessfully [10]. Grafting of THF from epoxidized butyl rubber also was unsuccessful. It was proposed that the steric hindrance of the substituted epoxides prevented the initiating activity. Less substituted epoxides were found to be reactive, but the products were ill-defined because of side reactions.

The mechanism of epoxide polymerization is still controversial with both S$_N$1 and S$_N$2 mechanisms suggested for ring-opening upon acidic cleavage of epoxides [6]. A competitive scheme was suggested for the acidic cleavage of substituted epoxides, as shown in Scheme 3; the intermediate oxonium ion can undergo an S$_N$1 reaction to form carbenium ions, while the S$_N$2 mechanism results in opening the epoxy rings without carbocation formation.

It is also known that epoxides are prone to rearrangement under the influence of Lewis acids, forming the corresponding aldehydes, ketones or dioxanes etc. [11–13]. The ring-opening mechanism of styrene epoxide (SE, 1), as shown in Scheme 4, was based on the study of Friedel–Crafts alkylation in the presence of SnCl$_4$ in toluene at 0 °C [14]. 2 and 3 are produced by the formation of secondary carbocations via S$_N$1 mechanism, 4
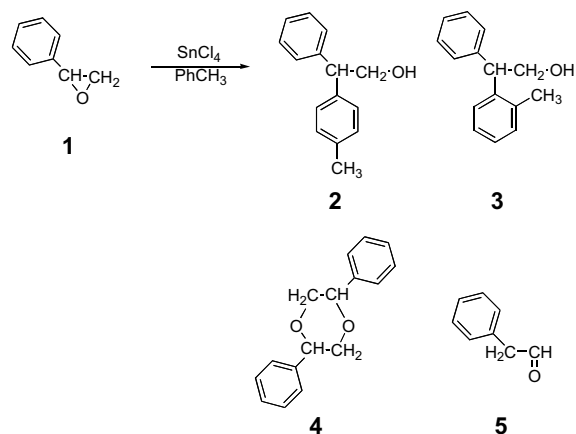
Scheme 4. Ring opening of styrene epoxide by SnCl$_4$ [14].

is a cyclic dimer of **1**, and **5** is an isomerization product. The product distribution of **2/3/4/5** was found to be 31:12:13:33 by GC analysis. It can be seen from the product ratios that the rates of dimerization/isomerization (i.e., the production of benzaldehyde and dioxane) was comparable to the rate of carbocation formation. In the case of MSE, isomerization to aldehyde reportedly occurs even during distillation [15].

Since structure is an important factor in the reactivity of epoxides, and most likely in the relative extent of S_N1 and S_N2 pathways when reacted with Lewis acids, we decided to investigate the effect of chemical structure of styrene-based epoxides on the initiation of IB polymerization. In this paper, the effectiveness of styrene-based epoxides (SE, *p*-methylstyrene epoxide (pM-SE) and α-methyl-*p*-methylstyrene epoxide (pM-MSE)) as carbocationic initiators of IB polymerization in conjunction with TiCl$_4$ will be reported, in comparison with MSE. The one-step synthesis and characterization of PIB carrying one *primary* hydroxyl head group and one *tertiary* chloride end group will also be reported.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich, Milwaukee, WI unless stated otherwise. MSE, SE, pM-SE and pM-MSE were synthesized from their corresponding olefins, α-methyl styrene, styrene, *p*-methyl styrene and *p*-methyl-α-methylstyrene respectively, with purified 3-chloro-peroxybenzoic acid (*m*-CPBA) as described in the literature [1,5]. All olefins were purified by vacuum distillation prior to use.

Isobutylene (IB, BOC) and methyl chloride (MeCl, BOC) were dried by passing them through a BaO and a CaCl$_2$ column. Hexane (Hx) was purified by distillation from Na/benzophenone. Titanium tetrachloride (TiCl$_4$) and di-*tert*-butylpyridine (D*t*BP) were used as received.

2.2. Polymerization

The polymerization reactions were carried out in an Mbraun LabMaster 130 glove box equipped with an integral cold hexane bath chilled with an FTS Flexi Cool immersion cooler. The moisture (<1 ppm) and oxygen (<5 ppm) contents were monitored. A 500 ml, round-bottom flask equipped with an overhead stirrer was charged with MeCl and Hx (40/60 v/v). D*t*BP was introduced to the mixture and allowed to stir for 10 min, followed by the addition of the initiator and IB (the concentrations are specified in the text or figure legends). The solution mixture was then stirred for 30 min. Separately, a 1 M TiCl$_4$ stock solution was prepared and pre-chilled to −80 °C. The polymerization commenced

with the rapid introduction of the appropriate amount of TiCl$_4$ stock solution. Aliquots of known mass were removed from the reactor at predetermined times into chilled culture tubes containing methanol for gravimetric conversion and size exclusion chromatography (SEC) analysis. The reactions were terminated at specified times by the addition of methanol to the charges. The solvents were evaporated, and the polymers were re-dissolved in hexane, washed with distilled water and dried over MgSO$_4$. The filtered polymer solution was then precipitated from methanol, chilled with dry ice and washed with methanol. The purified polymer was dried in a vacuum oven, and final conversion was determined gravimetrically.

2.3. Polymer characterization

Molecular weights (MW) and molecular weight distributions (MWD) were determined by SEC using a Waters system, equipped with six Styragel HR columns (pore sizes = 100, 500, 10^3, 10^4, 10^5, and 10^6 Å) thermostated at 35 °C, a Dawn DSP 18-angle laser light scattering detector (Wyatt Technology), a Waters 410 DRI detector thermostated at 40 °C, and a Waters 484 Tunable Absorbance Detector. THF, continuously distilled from CaH$_2$ was employed as a mobile phase and was delivered at 1 ml/min. ASTRA (Wyatt Technology) was used to obtain absolute MW data with $dn/dc = 0.093$ for PIB in THF.

The ^{1}H-NMR spectra of the samples in CDCl$_3$ or CD$_2$Cl$_2$ were recorded on a Mercury 400-MHz spectrometer.

FTIR spectra (4 cm^{-1} resolution, 32 scans) were recorded on a Bio-Rad FTS 175 FTIR spectrophotometer, using a 50-mm path length cell with 1–5 mM polymer solution in CCl$_4$.

3. Results and discussion

3.1. Effect of epoxide structure on the initiation efficiency

Scheme 5 shows the chemical structure of the epoxide initiators used in our study. The MSE/TiCl$_4$ initiation
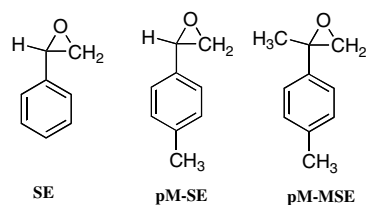
Scheme 5. Structure of styrene-based epoxides used in this study.

system has been investigated in detail, revealing living carbocationic polymerization of IB, i.e. linear M_n-conversion plots, first-order kinetics of monomer consumption and narrow MWD polymers, in the −80 to −60 °C range [1–4]. When the epoxide ring opens, MSE will yield a *tertiary* carbocation, while SE will yield a *secondary* carbocation via S_N1 mechanism (see Scheme 2). Introducing a methyl group in *para* position of the aromatic ring (pM-MSE and pM-SE) would be expected to stabilize the corresponding carbocations via a positive inductive effect. However, hyperconjugation between the *para*-substituent and the π-electron sextet of the aromatic ring would have a destabilizing effect. Steric effects may also play a role.

Fig. 1 shows M_n-conversion plots for SE, pM-SE and pM-MSE.

In living polymerization, M_n increases linearly with conversion, and I_{eff} can be determined from the ratio of the slope of linear M_n-conversion plots and the slope of the theoretically expected line, shown in Fig. 1. It can be seen that SE and pM-MSE had linear M_n-conversion plots, but these ran well above the theoretical line, indicating low I_{eff} values. $I_{eff} = 8\%$ and 30% was calculated for SE and pM-MSE, respectively. The low I_{eff} resulted from the loss of these epoxides due to side reactions during ring opening, such as the formation of dioxanes, aldedydes and polyethers from competition between S_N1 and S_N2 pathways as shown in Schemes 2 and 4. Since I_{eff} is defined as the percentage of the initiator that yields carbocations to induce IB polymerization, the relative proportion of the simultaneous reactions in the epoxy-ring opening reaction was apparently influenced by the epoxide structure. Compared to SE, the methyl substituent in pM-MSE increased the proportion of carbocations through steric strain and electron-donating stabilization, showing I_{eff} values comparable to MSE. However, the *p*-methyl substituent

Fig. 2. First-order rate plots of IB polymerizations with various epoxide initiators. Polymerization conditions are given in Fig. 1.

alone in pM-SE, resulted in non-linear M_n-conversion plot and lower I_{eff} (20–30%). Fig. 2 shows the first-order rate plots for the various initiators. SE has a linear plot, similar to that reported for MSE [1,4], revealing first-order kinetics of monomer consumption, whereas both pM-SE and pM-MSE-initiated IB polymerizations deviated from first-order kinetics. Non-linear semilogarithmic rate plots imply non-living conditions.

The results presented above show that both aromatic nucleophilicity and steric strain are important factors in promoting carbocation formation in the cleavage of epoxides by $TiCl_4$, that in turn initiate the cationic polymerization of IB.

Fig. 3 shows the molecular weight distribution (MWD)–conversion plots. SE and pM-MSE yielded very narrow final distribution (MWD < 1.05) and decreasing MWDs with increasing conversion, as expected in the living polymerization. pM-SE yielded somewhat broader distribution throughout the polymerization.
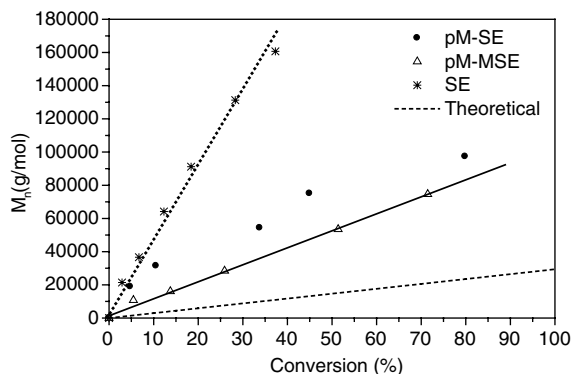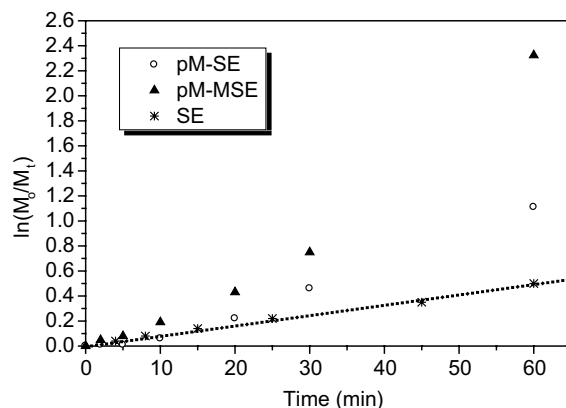

Fig. 1. M_n vs. conversion plot of IB polymerizations with various epoxide initiators. Hx/MeCl = 60/40 (v/v); $T = -80$ °C; $[\text{epoxide}]_0 = 4.0 \times 10^{-3}$ M; $[\text{IB}]_0 = 2.0$ M; $[\text{D}t\text{BP}] = 7.0 \times 10^{-3}$ M; $[\text{TiCl}_4] = 0.064$ M.
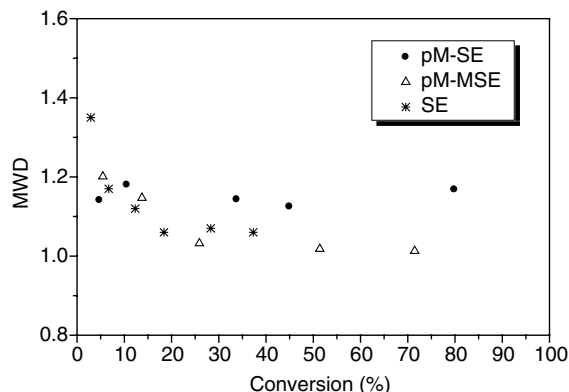

Fig. 3. MWD vs. conversion plots of IB polymerizations with various epoxide initiators. Polymerization conditions are given in Fig. 1.

The results above demonstrate that SE/TiCl$_4$ initiated the living polymerization of IB. pM-MSE/TiCl$_4$ showed linear M_n-conversion plot and decreasing MWD with conversion, characteristics of living polymerizations, but its semilogarithmic rate plot deviated from linearity. The reason for this is unknown at this time, and may be related to the presence of a contaminant during synthesis. More detailed investigations will be carried out with pM-MSE. Considering the low initiation efficiency with SE/TiCl$_4$, MSE/TiCl$_4$ should be the initiator of choice for the living carbocationic polymerization of IB on a pilot scale.

3.2. Scale-up of the synthesis of α-primary-hydroxyl-ω-tertiary-chloride telechelic PIB with MSE/TiCl$_4$—one-step functionalization

Experiments were carried out to scale up the polymerization procedure for the direct hydroxyl-functionalization of polyisobutylenes (PIB-OH) to produce low MW PIB-OH (M_n = 5000–10,000 g/mol). The most important factor to be considered is heat transfer. The rate constant of propagation in carbocationic IB polymerization is $k_p = 10^8$ l/mol s [16] so the release of the heat of polymerization is very rapid. This poses a scale-up problem because, maintaining close to isothermal conditions is becoming more difficult with increasing reactor volume. Another problem is that increasing the initiator to monomer ratio decreases I_{eff} [1–3]. One approach is to use high monomer concentration with low initiator concentration, and stop the reaction at low conversion. Polymerizations were carried out in both 500 and 5000 ml reaction flasks for comparison; conditions are given in Table 1.

The reactions **A** and **D** were stopped at about 10% conversion. Polymer MWs and MWDs determined by SEC are given in Table 2. No significant difference was found between the smaller and larger scale experiment (**D** and **A**). In experiment **B**, the reaction was stopped at 24% conversion, yielding higher molecular weight PIB-OH.

Twenty-four separate experiments were carried out under condition **A** in order to investigate the reproduc-

Table 2
Characterization of PIB-OH polymers

Reaction conditions	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_w/M_n
A	5200	5600	5900	1.08
B	12000	13000	14000	1.08
C	5200	6600	7600	1.27
D	5300	5600	5900	1.06

ibility of the synthesis procedure, and all polymers were characterized. The incorporation of the MSE fragment into the polymers was demonstrated by SEC, as shown in Fig. 4. Since PIB is UV-transparent, the UV signal of the polymer sample corresponding well to the refractive index (RI) signal throughout the distribution indicates even distribution of the aromatic ring of the initiator in the polymer.

The incorporation of MSE into the polymer chain was further confirmed by NMR as reported [4]. Fig. 5 shows a representative ^{1}H-NMR spectrum. The aromatic protons of the MSE (e) can be seen between 7.1 and 7.4 ppm. The two doublets at 3.4 and 3.6 ppm were assigned to the –CH$_2$ protons adjacent to the –OH (a).
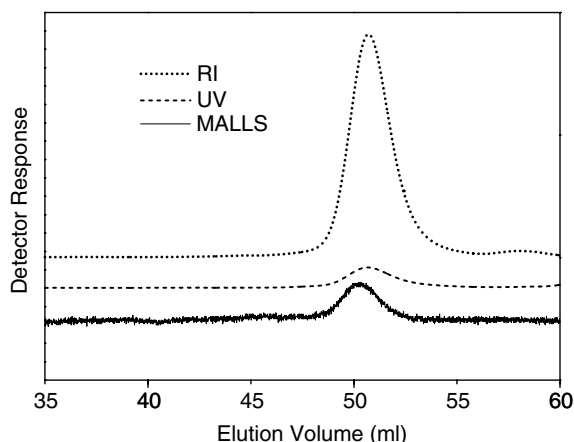
Fig. 4. SEC traces of a representative PIB-OH sample with triple detection (RI, UV and MALLS).

Table 1
Polymerization conditions

Condition	A	B	C	D
[DtBP] (mol/l)	0.007	0.007	0.007	0.007
[MSE] (mol/l)	0.019	0.019	0.1	0.019
[IB] (mol/l)	2.1	2.1	1.8	2.1
[TiCl$_4$] (mol/l)	0.064	0.064	0.2	0.064
Temperature (°C)	−60	−70	−50	−60
Reaction time (min)	10	20	10	10
Reaction volume (ml)	5000	5000	500	500
Yield (%)	10	24	58	10

Fig. 5. ^{1}H-NMR spectrum of a representative PIB-OH sample.
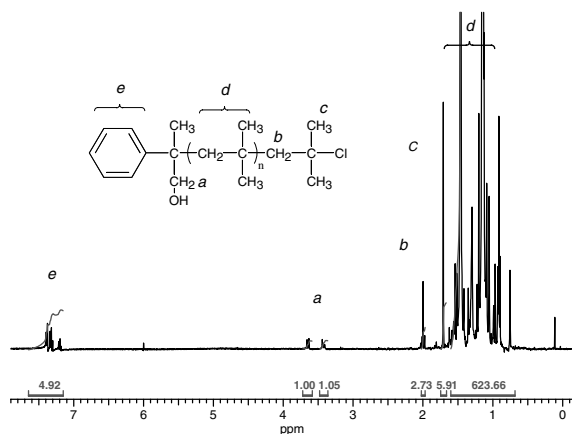

Fig. 6. IR calibration curve with PPOH in CCl$_4$. Inset: IR spectrum of a representative PIB-OH sample in CCl$_4$.

The signals of the two gem-dimethyl protons next to the *tert*-chloride end groups (c) appear at 1.64 ppm [17]. The 5/2/6 ratio of these signals demonstrates quantitative functionalization in each of the 24 cases—thus each PIB molecule carries one *primary* hydroxyl head group attached to the aromatic MSE-fragment, and one *tert*-chloride end group.

The signal of the –CH$_2$– group adjacent to the quaternary carbon of the end group (b in Fig. 5) is expected to appear at 1.9 ppm [17]. The b/c ratio was found to be consistently higher than the expected 1/3, indicating the presence of an overlapping signal so this signal was not used for functionality determination. Functionality was also calculated from the integration of the signal of the two protons adjacent to the –OH from 3.4–3.7 ppm (a) and the protons of the CH$_2$ and CH$_3$ groups of the main chain from 0.5–2.0 ppm (d), coupled with molecular weight data as shown in Eq. (1):

$$F_n = (A_a/2)/(A_d/8n) \qquad (1)$$

where A_a and A_d are the integrals corresponding to protons a and d, respectively, and n is the degree of polymerization obtained from SEC data. This method yielded $F_n = 1.09 \pm 0.16$ from the 24 experiments.

The quantitative analysis of the OH-functionalized PIBs was also carried out by FTIR analysis using 2-phenyl-1-propanol (PPOH) for calibration, since the polymer molecular weight does not affect IR absorptivity [10]. In order to avoid hydrogen-bonding, very dilute solutions (1–5 mM) and a long-path-length (50 mm) FTIR cell were used for IR analysis. The IR peak at 3640 cm^{-1} corresponds to the OH stretching mode of the free OH group, whereas another overlapping peak at 3604 cm^{-1} was assigned to intramolecular hydrogen bonding of the –OH groups to the aromatic ring. The calibration curve shown in Fig. 6 was based on the absorbance at 3640 or 3604 cm^{-1} against the correspond-

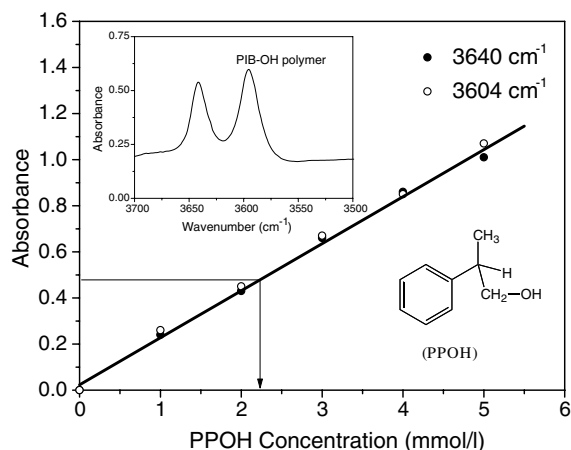ing concentration. In comparison with PPOH, PIB-OH has higher intensity at 3604 cm^{-1} than at 3640 cm^{-1}, due to higher electron density of the aromatic ring resulting from the I+ effect of the long polymer chain. Therefore, the peak height at 3640 cm^{-1} was selected for the determination of OH concentration of the polymer, using Eq. (2) [4]:

$$F_n = [P]_{IR}/[P]_{SEC} \qquad (2)$$

where $[P]_{IR}$ and $[P]_{SEC}$ is the polymer concentration based on FTIR analysis and SEC, respectively.

FTIR analysis was carried out on eight samples, yielding $F_n = 1.30 \pm 0.12$. This value is somewhat higher than that obtained by NMR. The reason for this discrepancy is not clear at this time, but might be attributed to the presence of trace amounts of methanol, which is very difficult to remove from PIB, and error in the IR calibration and/or molecular weight measurement.

PIB-OH with $M_n = 5000$ g/mol was also synthesized with high initiator concentration (experiment **C** in Tables 1 and 2). However, in this case the polymerization rate increased dramatically as a result of high initiator concentration, even at the 500 ml scale, and the polymerization heat released could not be removed fast enough from the system. The reaction temperature within the flask increased to above −40 °C where IB polymerization was not living [4]. High temperature promotes side reactions, leading to non-living conditions and ill-controlled initiation. Indeed, the OH functionality of this polymer was $F_n = 0.75$ and 0.79 by NMR and FTIR, respectively. Therefore the critical factor in scale-up is maintaining $T < -50$ °C in the reaction vessel. This can be achieved with lower starting temperature, or more efficient heat removal.

In summary, the TiCl$_4$/MSE system successfully initiated the IB polymerization at −50 to −70 °C on a pilot

scale, to yield PIB carrying one *primary* hydroxyl head group and one *tertiary* Cl group. PIB-OH prepared with high initiator concentration had lower hydroxyl functionality ($F_n < 0.8$), most likely resulting from side reactions caused by elevated temperatures that occurred during extremely rapid polymerization. In order to produce low molecular weight polymers with high yield and narrow molecular weight distribution on the scale of pound per batch, it is essential to effectively remove the heat build-up by rapid polymerization in order to maintain living conditions. With this, hydroxyl-functionalized PIB with desired molecular weight and functionality, and narrow molecular weight distribution can readily be synthesized.

4. Conclusions

We have demonstrated the effect of the structure of styrene-based epoxides on the initiation of carbocationic IB polymerization in conjunction with $TiCl_4$. SE initiated the living carbocationic polymerization of IB, but initiator efficiency was low in comparison with MSE ($I_{eff} = 8\%$ and 35%, respectively). The polymerization initiated by pM-SE was non-living, while pM-MSE yielded linear M_n-conversion plot but non-linear semi-logarithmic conversion plot. Among the epoxides investigated, MSE was the best initiator to synthesize functionalized PIB on a pilot scale in one step, with the PIB having one *primary* hydroxyl head group and one *tertiary* chloride end group, low molecular weight and narrow molecular weight distribution.

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