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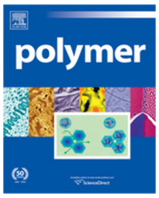

Room temperature living cationic polymerization of styrene with HX-styrenic monomer adduct/$FeCl_3$ systems in the presence of tetrabutylammonium halide and tetraalkylphosphonium bromide salts

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ABSTRACT

Living cationic polymerization of styrene was achieved with a series of initiating systems consisting of a HX-styrenic monomer adduct (X = Br, Cl) and ferric chloride ($FeCl_3$) in conjunction with added salts such as tetrabutylammonium halides ($n\mathrm{Bu_4N^+Y^-}$; $Y^- = Br^-, Cl^-, I^-$) or tetraalkylphosphonium bromides [$n\mathrm{R'_4PBr}$; R′ = CH_3CH_2–, $CH_3(CH_2)_2CH_2$–, $CH_3(CH_2)_6CH_2$–] or tetraphenylphosphonium bromide [$(C_6H_5)_4PBr$] in dichloromethane (CH_2Cl_2) and in toluene. Comparison of the molecular weight distributions (MWDs) of the polystyrenes prepared at different temperatures (e.g., −25 °C, 0 °C and 25 °C) showed that the polymerization is better controlled at ambient temperature (25 °C). The polymerization was almost instantaneous (completed within 1 min) and quantitative (yield ~100%) in CH_2Cl_2. In CH_2Cl_2, polystyrenes with moderately narrow ($M_w/M_n \sim 1.33$–1.40) and broad ($M_w/M_n \sim 1.5$–2.4) MWDs were obtained respectively with and without $n\mathrm{Bu_4N^+Y^-}$. However, in toluene, the MWDs of the polystyrenes obtained respectively with and without $n\mathrm{Bu_4N^+Y^-}/n\mathrm{R'_4P^+Br^-}$ were moderately narrow ($M_w/M_n = 1.33$–1.5) and extremely narrow ($M_w/M_n = 1.05$–1.17). Livingness of this polymerization in CH_2Cl_2 was confirmed via monomer-addition experiment as well as from the study of molecular weights of obtained polystyrenes prepared simply by varying monomer to initiator ratio. A possible mechanistic pathway for this polymerization was suggested based on the results of the ^1H NMR spectroscopic analysis of the model reactions as well as the end group analysis of the obtained polymer.

1. Introduction

Ever since their discovery in the 1950s living polymers have played a central role in polymer science and technology because of their wide range of applications [1–3]. In particular, the ionic “living” polymerization process unifies a number of attractive features, such as predictable polymer length combined with high monodispersity, end group functionality and stereoregularity. Among “living” polymerization techniques, cationic polymerization is limited to only certain vinyl monomers such as styrene [4–8], substituted styrenes [9–13], vinyl ethers [14–16] and isobutene [17–20]. Strongly electron-donating groups present on these vinyl monomers stabilize the propagating carbocationic species and enhance their reactivity to undergo cationic polymerization reaction. But styrene, when polymerized with conventional cationic initiators, forms an unstable growing carbocation that is prone to undergo chain transfer, chain termination and other undesirable side reactions [21] leading to the formation of polystyrenes with broad molecular weight distributions (M_w/M_n). As a result, at least theoretically, cationic polymerization of styrene with conventional cationic initiators has been considered difficult [22]. Therefore, specially designed initiating systems have been used to achieve living cationic polymerization of styrene as reported by many researchers [5,7,8,23–27]. For example, Higashimura and his coworkers were the first to report cationic polymerization of different vinyl monomers that occurs in a controlled manner [23]. They were also the first to report “living” cationic polymerization of styrene using methanesulfonic acid/tin tetrachloride ($CH_3SO_3H/SnCl_4$) initiating system with tetrabutylammonium chloride ($n\mathrm{Bu_4NCl}$) in CH_2Cl_2 [24]. Subsequently, they have also reported cationic polymerization of styrene using other initiating systems [5,25]. But, none of the initiating systems contain ferric chloride ($FeCl_3$). Following these works, several other research groups have reported cationic polymerization of styrene using $TiCl_4$ at −80 °C [7,26] and at −70 °C [8,27]. However, in all of these cases, the molecular weight distributions (MWDs) of the obtained polymers are quite broad [polydispersity index (PDI) = $M_w/M_n = 1.8$, [7] 1.37, [26] 1.31 [8] and 1.46 [27]]. Matyjaszewski and his associates used

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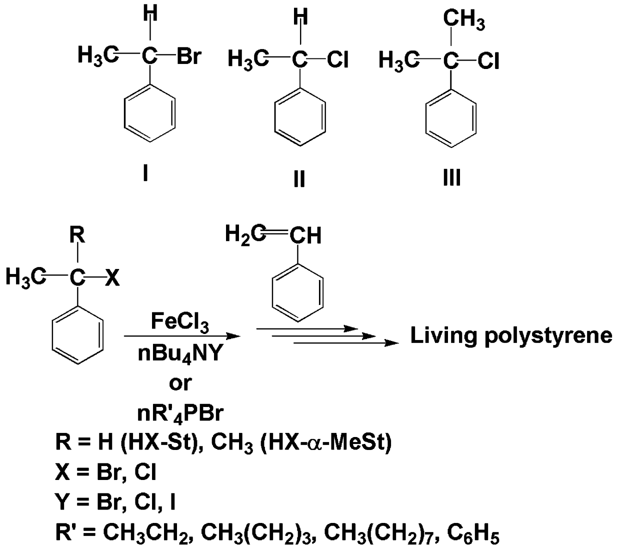
boron trichloride (BCl_3) to carry out cationic polymerization of styrene at −75 °C, but the obtained polystyrenes had broad PDIs (≥1.3) [28]. However, polystyrene with narrow MWD (PDI ∼ 1.1) has been synthesized through cationic polymerization of styrene using $TiCl_3(OiPr)$ [titanium(IV) chloride substituted with an electron-donating isopropoxy group] at −78 °C [29].

A detailed survey of the literature shows that there have been very few reports regarding the use of $FeCl_3$ as an activator or as one of the components of the initiating systems in the cationic polymerization of vinyl monomers. These are cationic polymerization of 1,3-pentadiene with $FeCl_3$ in *n*-hexane at 0 °C and at room temperature [30], cationic polymerization of isobutyl vinyl ether using "$FeCl_3$/added base" initiating system at 0 °C in toluene [31], cationic polymerization of styrene with $FeCl_3$ in liquid SO_2 at 0 °C [32] and electroinitiated cationic polymerization of styrene using $FeCl_3$ in acetone at 0 °C [33]. According to these reports, cationic polymerization of styrene with $FeCl_3$ was poorly controlled. Although, there have been some reports that described the cationic polymerization of styrene and other vinyl monomers using "$SnCl_4$/added salt", [5,6,25] "$TiCl_4$/added salt" [7,34] and "$TiCl_3(OiPr)$/added salt" [29], but, the system comprising of $FeCl_3$ and an added halide salt has never been used to initiate cationic polymerization of styrenic monomers. Although, one recent report shows the use of initiating system comprising of $FeCl_3$ and nBu_4NCl for cationic polymerization of isobutyl vinyl ether in CH_2Cl_2 at 0 °C. But, in this case, the obtained polymers showed broad MWDs (PDI ≥ 1.67) [31]. Again, to the best of our knowledge, there are no reports of cationic polymerization of styrene at or near room temperature (25 °C).

The objective of this work is to develop new $FeCl_3$ based initiating systems for truly "living" cationic polymerization of styrene at room temperature (25 °C). Thus, herein, we report the systematic study on the cationic polymerization of styrene employing a series of initiating systems consisting of a HX-styrenic monomer adduct [e.g., $C_6H_5(CH_3)CHBr$ (**I**) or $C_6H_5(CH_3)CHCl$ (**II**) or $C_6H_5C(CH_3)_2Cl$ (**III**)] as the alkyl halide type initiators coupled with a strong Lewis acid ($FeCl_3$) as the activator and an externally added salt [tetrabutylammonium halide, nBu_4NY; Y = Br, Cl, I or tetraalkylphosphonium bromide, nR'_4PBr; R′ = CH_3CH_2–, $CH_3(CH_2)_2CH_2$–, $CH_3(CH_2)_6CH_2$– or tetraphenylphosphonium bromide, $(C_6H_5)_4PBr$] at room temperature (25 °C) in CH_2Cl_2 and in toluene. The chemical structures of all the initiators and polymerization reaction are schematically shown in Scheme. 1.



Scheme 1. Living cationic polymerization of styrene using HX-styrenic monomer adduct/FeCl3 in the presence of added salt.

To explore the nature of the propagating species, model reactions were also designed by mimicking the reaction conditions of the polymerization reactions, but in the absence of the monomer. A possible mechanism of this "living" cationic polymerization is discussed based on the results of the ^1H NMR spectroscopic analysis of these model reactions.

2. Experimental

2.1. Materials

Styrene (St) (Aldrich, purity ≥ 99%) and α-Methylstyrene (α-MeSt) (Aldrich, purity > 99%) were washed with 5 wt% aqueous NaOH solution to remove the inhibitor, dried overnight with calcium chloride ($CaCl_2$) and then distilled over calcium hydride (CaH_2) under reduced pressure prior to use. (1-Bromoethyl)benzene (Aldrich, purity 97%) was used as received. Anhydrous ferric chloride ($FeCl_3$) (Merck, India, purity 96%) was used as received. Tetrabutylammonium bromide, $[CH_3(CH_2)_3]_4NBr$ (Aldrich, purity ≥ 99%), tetrabutylammonium chloride, $[CH_3(CH_2)_3]_4NCl$ (Aldrich, purity ≥ 99%), tetrabutylammonium iodide, $[CH_3(CH_2)_3]_4NI$ (BDH laboratory reagents, England, purity 98%), tetraethylphosphonium bromide, $(CH_3CH_2)_4PBr$ (Aldrich, purity 97%), tetrabutylphosphonium bromide, $[CH_3(CH_2)_3]_4PBr$ (Aldrich, purity 98%), tetraoctylphosphonium bromide, $[CH_3(CH_2)_7]_4PBr$ (Aldrich, purity 97%), tetraphenylphosphonium bromide, $(C_6H_5)_4PBr$ (Aldrich, purity 97%) were used without any purification, but after drying in vacuum at 35 °C for 6 h before use.

All the solvents were of reagent grade and were purchased from Merck, India. First, dichloromethane (CH_2Cl_2) (Merck, India) was washed with concentrated H_2SO_4 (thrice, 30 mL acid per 100 mL), then successively with water (once), 5 wt% aqueous NaOH solution (twice) and then again with distilled water (thrice), dried overnight over anhydrous $CaCl_2$ and distilled over phosphorous pentoxide (P_2O_5) just before use in the polymerization process. Toluene was purified by shaking twice with concentrated H_2SO_4 (100 mL of acid per litre of toluene), once with water, once with aqueous 5% NaOH solution and then with water. It was then refluxed over sodium/benzophenone under nitrogen atmosphere and distilled prior to use in the polymerization reaction.

2.2. Synthesis of HX-styrenic monomer adducts

The HBr-styrene (HBr-St) adduct (**I**) was obtained from commercial source (see Scheme 1 for chemical structure). The HCl-styrene adduct (**II**) and HCl-α-methylstyrene adduct (**III**) (see Scheme 1) were synthesized by bubbling dry HCl gas into a 1.0 M CH_2Cl_2 solution of styrene and α-methylstyrene respectively for 5 h at 0 °C [8,26,35]. HCl gas was generated by dropping concentrated sulphuric acid into powdery sodium chloride and was passed through a column packed with anhydrous $CaCl_2$ for drying. After 5 h of reaction, the excess HCl gas was removed by bubbling dry nitrogen gas into the reaction mixture. The clean and quantitative formation of adducts **II** and **III** were confirmed via ^1H NMR and ^{13}C NMR spectroscopy (see Fig. S1–S4 in ESM). The adducts were isolated by evaporating the solvents in a rotary evaporator. Finally, the isolated adducts were vacuum distilled from CaH_2 to obtain the pure HCl adducts (**II** and **III**) and were stored under nitrogen in a freezer that were used in the subsequent polymerization reaction.

2.2.1. HCl-styrene adduct (II)

^1H NMR (300 MHz, $CDCl_3$, δ ppm): 1.86–1.88 (d, 3H, CH_3), 5.08–5.14 (q, 1H, CH), 7.29–7.45 (m, 5H, aromatic CH); ^{13}C NMR (300 MHz, $CDCl_3$, δ ppm): 26.64 (CH_3), 58.89 (C–Cl), 126.62, 128.36, 128.75 (aromatic CH), 142.95 (aromatic C).

2.2.2. HCl-α-methylstyrene adduct (***III***)

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.04 (s, 6H, CH_3), 7.26–7.65 (m, 5H, aromatic CH); ^{13}C NMR (300 MHz, $CDCl_3$, δ, ppm): 34.38 (CH_3), 69.68 (C–Cl), 125.53, 127.63, 128.32 (aromatic CH), 146.37 (aromatic C). These data matches with those reported for the same compound published elsewhere [36].

2.3. Polymerization procedure

All polymerizations were performed under dry nitrogen in a 25 mL two-necked round-bottomed flask equipped with a three-way stopcock attached to a nitrogen gas filled balloon in one neck and a silicone rubber septum in the other. The concentrations of monomer (styrene) and the initiator adducts (**I**–**III**) were kept constant at 1.0 M and 20 mM respectively. The parameters that were varied are the concentrations of the Lewis acid activator ($FeCl_3$) and the added halide salts to examine the effect of their concentrations on the molecular weights and molecular weight distributions (MWDs) of the obtained polystyrenes. Polymerization reactions were performed in two different solvents, dry CH_2Cl_2 and dry toluene. The following is a typical polymerization procedure: nBu$_4$PBr (108.59 mg, 0.32 mmol) was taken in a double necked reaction flask and was evacuated through a high vacuum pump for 6 h and was sealed with a silicone rubber septum after back filling with nitrogen. Dry CH_2Cl_2 (7.0 mL), previously purged with ultra high pure nitrogen gas, was then injected into the reactor by a syringe. The reaction mixture was further purged with nitrogen for 10 min to remove any dissolved gas present in CH_2Cl_2. The reactor containing the mixture was placed into a water bath made up of double walled water jacket glass vessel maintained at a temperature of 25 °C and the mixture was stirred magnetically. HBr-styrene adduct (**I**) i.e., (1-Bromoethyl)benzene (28 μL, 0.205 mmol) and styrene (1.0 mL, 8.728 mmol) were then injected separately into the reactor with a dry syringe through the septum. Finally, the polymerization was initiated by rapidly injecting a solution of anhydrous $FeCl_3$ (129.9 mg, 0.8 mmol) in CH_2Cl_2 (1.0 mL). During the polymerization, the reaction mixture was maintained stirring magnetically.

Polymerization reaction was terminated by addition of excess prechilled methanol containing a small amount of ammonia (0.1% v/v). The quenched reaction mixture was sequentially washed with 2 N hydrochloric acid, 10% aqueous NaOH solution and then with triple distilled water to remove any $FeCl_3$ present. The conversion of styrene was measured by gravimetry after isolating the obtained polystyrenes via solvent evaporation under reduced pressure and overnight drying in vacuum oven at 60 °C.

2.4. Characterization

2.4.1. NMR spectroscopy

^{1}H NMR and ^{13}C NMR spectra of all the synthesized initiators (adducts **II** and **III**), products of the model reactions and the obtained polystyrenes were recorded at 25 °C on a Bruker DPX 300 MHz spectrometer using $CDC1_3$ as the solvent and TMS as the internal reference.

2.4.2. GPC measurements

The number average molecular weight (M_n) and polydispersity index (PDI) of the purified polystyrenes were measured by size-exclusion chromatography using a Waters 1515 isocratic HPLC pump connected to three Waters Styragel HR1, HR3 and HR4 columns and a Waters 2414 Refractive Index Detector at room temperature (25 °C). HPLC grade THF was used as the eluent with a flow rate of 1 mL/min. The columns were calibrated against eight standard polystyrene samples with peak molecular weights (M_p) of 860, 1800, 3600, 8500, 19 100, 43 400, 50 000, and 100 000.

3. Results and discussion

3.1. Cationic polymerization of styrene using $FeCl_3$

Cationic polymerization of styrene was carried out using a series of new initiating systems consisting of various combinations of HX-styrenic monomer adducts [HBr-St (**I**): $C_6H_5CH(CH_3)Br$, HCl-St (**II**): $C_6H_5CH(CH_3)Cl$, and HCl-α-MeSt (**III**): $C_6H_5C(CH_3)_2Cl$] as the alkyl halide type initiators, a strong Lewis acid ($FeCl_3$) as the activator and externally added salts such as tetrabutylammonium halides (nBu$_4$NY; Y = –Br, –Cl, –I) or tetraalkylphosphonium bromides (nR$'_4$PBr: R$'$ = CH_3CH_2–, $CH_3(CH_2)_2CH_2$–, $CH_3(CH_2)_6CH_2$–) or tetraphenylphosphonium bromide, [$(C_6H_5)_4PBr$] as shown in Scheme 1.

Polarity of the solvent always plays a key role in the living cationic polymerization of any vinyl monomers. In cationic polymerization, with the increase of dielectric constant of the polymerization solvent, the rate of chain transfer to monomer and chain transfer to solvent decreases compared to the rate of propagation [37]. Generally, in a cationic polymerization reaction MWDs of the obtained polymers became progressively narrower with decreasing solvent polarity as reported by many researchers [38–40]. As usual in cationic polymerization, the reactions were faster in a more polar solvent. Thus, to examine the role of the solvent polarity, we performed polymerization in two different solvents, CH_2Cl_2, a relatively polar solvent and toluene, a non-polar solvent. The results of the cationic polymerization of styrene in these two solvents are discussed separately below.

3.1.1. Polymerization in CH_2Cl_2

3.1.1.1. Effect of initiator. $FeCl_3$ alone has been used very early as a catalyst for the cationic polymerization of styrene in liquid SO_2 medium at 0 °C [32]. However, they have not explored anything about the livingness of this polymerization. Later on, it has been reported that $FeCl_3$ alone is incapable of initiating polymerization of styrene in acetone [33]. These reports prompted us to study the cationic polymerization of styrene using $FeCl_3$ in more detail. To understand the system better, we investigated the effect of HX-styrenic monomer adducts (**I**, **II** and **III** see Scheme 1 for their chemical structure) as initiators and the added halide salt (A^+Y^-) on the kinetics and molecular weight distributions (MWDs) of the obtained polymers. To start with, first, we have conducted cationic polymerization of styrene with $FeCl_3$ in CH_2Cl_2 at 25 °C in absence of any initiator and added salts. The polymerization was instantaneous with a yield of 100% within 1 min. But, the MWD of the obtained polystyrene was very high (PDI = 2.62) (see entry 1 in Table 1). Thus, to control the MWDs of the obtained polystyrenes, we then introduced HX-styrenic monomer adducts (e.g., **I** or **II** or **III**) in the polymerization system as initiator. The reason for choosing such initiators is that they are structurally similar to the propagating species of the polymer end group. An important advantage of use of HCl-monomer adduct over other HX-monomer adducts (X = Br, I) is that the carbon-chlorine bond in the former adduct is relatively more stable compared to that of C–X bond present in later two adducts in inert atmosphere at room temperature. This makes the preparation, characterization and storage processes of well-defined multifunctional initiators much easier prior to the polymerization [41]. The polymerization result with these adducts are depicted in Table 1 and the corresponding GPC traces are presented in Fig. S5 of the ESM. In these cases, we also observed quantitative polymerization, ∼100% within 1 min (see Table 1). GPC traces of all the obtained polystyrenes using **I**, **II** and

Table 1
Polymerization data for styrene with $FeCl_3$ using different HX-adducts in presence and in absence of added salt.

Entry	HX-adduct	Added salt	Dichloromethane		Toluene	
			$M_{n,\ GPC}$	PDI	$M_{n,\ GPC}$	PDI
1	–	–	10504	2.62	2496	1.47
2	**I**	–	7696	2.41	1352	1.33
3	**II**	–	3952	2.25	3536	1.35
4	**III**	–	2600	1.46	1560	1.31
5	**I**	nBu_4NBr	13 208	1.48	1220	1.21
6	**II**	nBu_4NBr	2600	1.42	1040	1.19
7	**III**	nBu_4NBr	8112	1.40	1248	1.17

Polymerization condition: $[M]_0 = 1.0$ M; $[\mathbf{I–III}]_0 = 20$ mM; $[FeCl_3]_0 = 100$ mM; $[\text{added salt}]_0 = 40$ mM; Temperature = 25 °C; Time ~1 min (dichloromethane) and 48 h (toluene); Conversion ~100% (dichloromethane) and 72% (toluene).

III, are unimodal in nature (see Fig. S5 in ESM) with a PDI of 2.41, 2.25 and 1.46 respectively (see entries 2–4 in Table 1). It is interesting to note that these results clearly indicate that among all the three initiators, the initiator **III** produced polystyrene with the narrowest PDI (1.46, see entry 4 in Table 1). Such low PDI of the obtained polystyrenes (using **III**) may be attributed to the generation of a stable tertiary carbocation compared to that obtained using **I** and **II**, which generates secondary carbocation. But the exact reason of this observation is still under investigation.

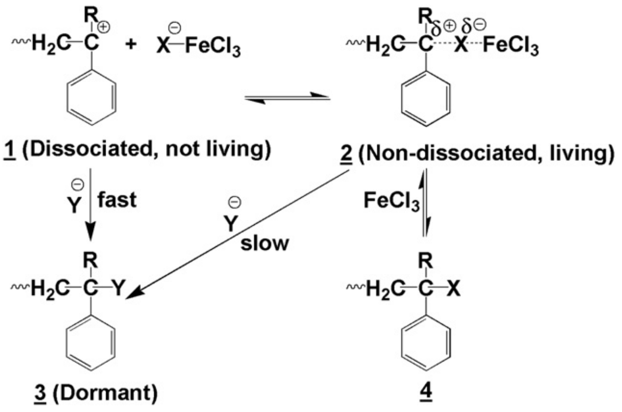
Again, it has been reported that in the cases of cationic polymerization of vinyl monomers using metal halide, the added salts such as tetraalkylammonium halide can reduce the PDI of the obtained polymer [5,6,25,31,34]. This study encouraged us to explore the effect of addition of salts such as tetraalkylammonium halide or tetraalkylphosphonium halide in this polymerization medium as added salts. For example, when nBu_4NBr was added in the above-mentioned systems as mentioned in entries 2–4 in Table 1, we found that the PDIs of the obtained polystyrenes reduced further (see entries 5–7 in Table 1). It is worth mentioning that the effect of the added salt, nBu_4NBr is prominent only in presence of the HX-monomer adduct. Note that the PDI of the polystyrene produced using $FeCl_3$/added salt was close to that obtained using $FeCl_3$ alone (2.62, see entry 1 in Table 1). From these results, we may conclude that the cationic polymerization of styrene with $FeCl_3$ can be better controlled using a combination of both HX-styrenic monomer adduct and nBu_4NBr than that using either initiator or salt. Since, adduct, **III** produced polymer with lowest PDI, we carried out rest of the polymerizations using **III** to examine the effect of the nature of the added salt and temperature.

3.1.1.2. Effect of added halide salts (nBu_4NY/nR'_4PBr). Polymerization reactions were further carried out using **III**/$FeCl_3$ in conjunction with three different tetrabutylammonium halide salts of varying counteranion ($nBu_4N^+Y^-$; $Y^- = Br^-, Cl^-, I^-$) to examine their effect on the MWDs of the obtained polymers. The obtained results are summarized in Table 2 and the corresponding GPC traces are shown in Fig. S6 in the ESM, which clearly shows unimodal molecular weight distribution in all cases. In all the three cases, the PDI of the obtained polystyrene were little bit lower compared to that obtained in absence of any salt (compare entry 1 with entries 2–4 in Table 2). The reason for this low PDI of the obtained polystyrenes using quaternary halide salt is as follows: It has been well accepted that the addition of quaternary salts reduce the PDIs of the polystyrenes obtained from cationic polymerization of styrene using tetrabutylammonium chloride (nBu_4NCl) [5–7,24,29,34,42] and also using different tetrabutylammonium halides ($nBu_4N^+Y^-$; Y– = I–, Br–, Cl–) [25]. According to their proposition, the high nucleophilicity of the halide anions appears to be the primary factor that controls the polymerization towards a truly living system [13,34,43]. Consequently, in our case, the low PDIs of the obtained polymers are explained schematically using the above-mentioned concepts (see Scheme 2). It is well known that $FeCl_3$ is a strong Lewis acid. Thus, it usually generates a binary counteranion –$ClFeCl_3^-$ in non-aqueous medium by abstracting Cl from the C–Cl bond of the HCl-α-MeSt adduct, **III**. Nucleophilicity of this anion is so low that it cannot stabilize the growing carbocation. Thus, a highly dissociated and nonliving species (see structure $\underline{1}$ in Scheme 2) is generated in absence of any externally added salt. However, in presence of an added salt, the counteranion of the salt (Y^-) binds to $FeCl_3$. As a result, the Lewis acidity of $FeCl_3$ is decreased due to the formation of a comparatively weakly acidic species $FeCl_3Y^-$. Thus, $FeCl_3Y^-$ induced a controlled dissociation of the C–Cl bond of the HCl-α-MeSt adduct, **III**, which may not be possible in absence of such species. Again, Y^- can also bind with the propagating carbocationic species $\underline{1}$ and $\underline{2}$ and converts them to a "Dormant" species $\underline{3}$ (see Scheme 2). In this way, the uncontrolled propagation via the nonliving, dissociated species $\underline{1}$ is eliminated in presence of salt and a living polymerization occurs selectively via

Table 2
Polymerization data for styrene using **III**/$FeCl_3$ system with different added salts.

Entry	Added salt	Dichloromethane		Toluene	
		$M_{n,\ GPC}$	PDI	$M_{n,\ GPC}$	PDI
1	–	2600	1.46	1560	1.32
2	nBu_4NBr	8112	1.40	1248	1.17
3	nBu_4NCl	1560	1.38	1040	1.05
4	nBu_4NI	2912	1.33	1144	1.08
5	nEt_4PBr	3328	1.83	1210	1.07
6	nBu_4PBr	3224	2.00	1144	1.10
7	$nOct_4PBr$	1872	1.41	1352	1.16
8	Ph_4PBr	4992	1.78	1280	1.11

Polymerization condition: $[M]_0 = 1.0$ M; $[\mathbf{III}]_0 = 20$ mM; $[FeCl_3]_0 = 100$ mM; $[\text{added salt}]_0 = 40$ mM; Temperature = 25 °C; Time ~1 min (dichloromethane) and 48 h (toluene); Conversion ~100% (dichloromethane) and 72% (toluene).



Scheme 2. Possibility of formation of different living species in the cationic polymerization of styrene using HX-styrenic monomer adduct/FeCl3 in the presence of added salt.

the non-dissociated dormant species 3 [13]. So, the polymers with narrow MWDs, as obtained in the presence of added quaternary halide salts, are due to the suppression of the uncontrolled propagation, stabilization of the carbocationic centre and thus suppression of the chain transfer reactions [7]. It has been reported previously that addition of electron donors eliminates side reactions such as chain transfer, intramolecular alkylation by the growing cations and irreversible chain termination reaction [44].

It should be noted from the results depicted in entries 5–8 in Table 2 that the presence of quaternary phosphonium bromide salts instead of tetrabutylammonium halides does not improve the livingness of this polymerization system when all other reaction parameters are similar.

3.1.1.3. Effect of added halide salt concentration. Polymerization of styrene (1.0 M) with **III**/FeCl$_3$ (20 mM/100 mM) system was carried out at varying concentrations of added salt, *n*Bu$_4$NBr (ca. 0, 20, 40, 60 mM) to achieve the optimum reaction condition. The M_n and MWD values of the obtained polystyrenes are given in Table 3 (the corresponding GPC traces are shown in Fig. S7 in ESM), which suggested that the polymerization with **III**/FeCl$_3$ system produces polystyrene with narrowest MWD when an added salt (*n*Bu$_4$NBr) concentration of 40 mM was used (compare entry 3 with entries 1, 2 and 4 in Table 3). Hence, we conducted all the polymerizations using this salt concentration.

3.1.1.4. Effect of Lewis acid activator (FeCl$_3$) concentration. To check the effect of activator concentration on the polymerization of styrene in dichloromethane at 25 °C, four different sets of polymerization reactions (see Table 4) were also carried out using a fixed ratio of styrene/**III**/*n*Bu$_4$NBr = 1000/20/40 mM, but varying the FeCl$_3$ concentrations (ca. 0, 40, 100 and 150 mM). M_n and MWD values of the obtained polystyrenes are given in Table 4 (the corresponding GPC traces are shown in Fig. S8 in ESM), which suggested that the polymerization with **III**/*n*Bu$_4$NBr system produces polystyrene with narrowest MWD only at [FeCl$_3$] = 100 mM (compare entries 3 with 2 and 4 in Table 4). This is the reason why we have conducted all the polymerizations at this FeCl$_3$ concentration. Note that we did not observe any polymerization in absence of the Lewis acid activator, FeCl$_3$ (see entry 1 in Table 4).

3.1.1.5. Effect of temperature. According to the literature reports, cationic polymerization of styrene is usually better controlled at low temperature [4–8]. Thus, to check this low temperature effect in our case, we carried out polymerization reactions at −25 °C and 0 °C keeping all the other reaction parameters similar to that used at 25 °C. The molecular weights and MWDs of the obtained polystyrenes are given in Table 5 and the corresponding GPC traces of the polymers are presented in Fig. S9 in ESM. Again, the GPC traces are unimodal in nature. However, to our surprise, the MWDs of the polystyrenes obtained at −25 °C and 0 °C were relatively broader compared to that obtained for polystyrenes prepared at 25 °C (compare entry 3 with entry 1 and 2 and entry 6 with entry 4 and 5 in Table 5). The reason for such unusual broad MWDs of the obtained polymers is explained as follows: It has been mentioned that the chain transfer processes characteristically limit the molecular weight of the obtained polymers via cationic polymerization [40]. For styrenic monomers, alkylative attack on an aromatic group is thought to be the dominant chain transfers process [45,46]. In any polymerization system, the rate of chain transfer is usually higher at high temperature that resulted in broadening of the MWDs of the obtained polymers [47]. Therefore, in our case, one should expect to obtain polymers with broad MWDs at higher temperature (ca. 25 °C). But, we obtained polymers with broad MWDs at lower temperature (ca. −25 °C) and low MWDs at higher temperature (ca. 25 °C). Again, it has been reported for any cationic polymerization that the equilibrium between the dormant and the active species usually controls the MWDs of the obtained polymers. Faster equilibrium produced polymers with narrow MWDs [31]. On this basis, we propose that the broad MWDs are not due to the chain transfer reaction of the propagating carbocationic species, but possibly due to the slower interconversion between the dormant and the activated species at low temperature (ca. −25 °C) [6]. This is the reason why we conducted all the polymerization of styrene at room temperature (ca. 25 °C).

Table 3
Polymerization data for styrene using FeCl$_3$ at varying concentration of added salt, *n*Bu$_4$NBr.

Entry	[*n*Bu$_4$NBr]$_0$ (mM)	Dichloromethane		Toluene	
		$M_{n,\ GPC}$	PDI	$M_{n,\ GPC}$	PDI
1	0	2600	1.46	1560	1.32
2	20	2460	1.43	1300	1.22
3	40	8112	1.40	1248	1.17
4	60	17 200	1.45	1460	1.24

Polymerization condition: [M]$_0$ = 1.0 M; [**III**]$_0$ = 20 mM; [FeCl$_3$]$_0$ = 100 mM; Time ∼1 min (dichloromethane) and 48 h (toluene); Conversion ∼100% (dichloromethane) and 72% (toluene).

Table 4
Polymerization data for styrene using **III** and *n*Bu$_4$NBr system at different FeCl$_3$ concentrations.

Entry	[FeCl$_3$]$_0$ (mM)	Dichloromethane			Toluene		
		Conv. (%)	$M_{n,\ GPC}$	PDI	Conv. (%)	$M_{n,\ GPC}$	PDI
1	0	0	–	–	0	–	–
2	40	45	17 600	1.46	40	1040	1.22
3	100	100	8112	1.40	72	1248	1.17
4	150	70	2720	1.44	65	1310	1.31

Polymerization condition: [M]$_0$ = 1.0 M; [**III**]$_0$ = 20 mM; [added salt]$_0$ = 40 mM; Time ∼1 min (dichloromethane) and 48 h (toluene).

3.1.1.6. Polymer molecular weight control. It should be noted, that the polymerization of styrene in CH$_2$Cl$_2$ at 25 °C was very fast and the complete conversion was obtained within 1 min. Therefore, sampling or kinetic measurement during the polymerization had not been possible. Thus, to get further insight into the polymerization system, we carried out a series of polymerization reactions with **III**/FeCl$_3$/*n*Bu$_4$NI system simply by varying monomer to initiator ratio ([M]$_0$/[**III**]$_0$) from 50 to 200 and keeping the concentrations of FeCl$_3$ and *n*Bu$_4$NI constant at 100 mM and 40 mM respectively. The results of these polymerization systems are summarized in Fig. 1, which shows the plot of [M]$_0$/[**III**]$_0$ vs. M_n of the obtained polymers along with their corresponding GPC traces. It clearly reveals that M_n values of the obtained polystyrenes are in close agreement with that of the calculated values. Also, the M_n values of the polystyrenes increase almost linearly with increase of the feed ratio of monomer to initiator ([M]$_0$/[**III**]$_0$). The MWDs of the obtained polystyrenes (1.32–1.38) remains almost constant with increase of the feed ratio of monomer to initiator ([M]$_0$/[**III**]$_0$). Thus, we were able to produce polystyrenes of controlled molecular weight and MWDs by cationic polymerization of styrene using our initiating systems.

3.1.1.7. Monomer-addition experiment. Two-stage sequential monomer addition experiment for chain extension was carried out to establish the living nature of this styrene polymerization. The GPC traces of the polystyrenes obtained by chain extension

Table 5
Polymerization data for styrene using **III**/$FeCl_3$/added salt system at different polymerization temperatures.

Entry	Added salt	Temp. (°C)	Dichloromethane		Toluene	
			$M_{n,\ GPC}$	PDI	$M_{n,\ GPC}$	PDI
1	nBu$_4$NBr	−25	12 896	1.47	1210	1.24
2	nBu$_4$NBr	0	2490	1.45	1040	1.20
3	nBu$_4$NBr	25	8112	1.40	1248	1.17
4	nBu$_4$NI	−25	3341	1.69	1280	1.18
5	nBu$_4$NI	0	2680	1.44	1060	1.13
6	nBu$_4$NI	25	2860	1.33	1176	1.08

Polymerization condition: $[M]_0 = 1.0$ M; $[\textbf{III}]_0 = 20$ mM; $[FeCl_3]_0 = 100$ mM; $[\text{added salt}]_0 = 40$ mM; Time ~1 min (dichloromethane) and 48 h (toluene); Conversion ~100% (dichloromethane) and 72% (toluene).

experiment are shown in Fig. 2. A fresh feed of monomer ($[M]_0 = [M]_{add} = 1.0$ M) was added just before the initial charge of the styrene was completely polymerized to examine the livingness of the styrene polymerization by **III**/$FeCl_3$/nBu$_4$NI initiating system in CH_2Cl_2 at 25 °C. In the first stage, a conversion of 96% was reached after 1 min of polymerization and after the second stage the overall conversion was 194%. The M_n and PDI values for the two stages are $M_{n,}$(1st stage) = 2080, PDI = 1.33 and M_n (2nd stage) = 6240, PDI = 1.41 respectively. Both the GPC traces (Fig. 2) show unimodal distribution along with a clear lateral shift of maxima towards higher molecular weight region on going from stage-1 to stage-2. These results clearly indicate that the styrene polymerization with **III**/$FeCl_3$/nBu$_4$NI initiating system is living in a relatively polar solvent like CH_2Cl_2. However, the PDI of the polystyrene slightly increases after the addition of the second monomer feed, probably due to the slow initiation and slow exchange between reversibly terminated and propagating species [48].

From the above-mentioned results, it can be summarized that the cationic polymerization of styrene in CH_2Cl_2 with (**I**–**III**)/$FeCl_3$ system was instantaneous both in presence and in absence of added salt. Although the polymerization is living in nature, but is not well controlled. As a result, the MWDs of the obtained polystyrenes were broader (PDI ≥ 1.33) compared to that usually obtained in any well-controlled cationic polymerization system [5,6,24,25,29]. However, these reported polymerization systems are conducted either at 0 °C or even less up to −78 °C whereas we performed all the our polymerization reactions at room temperature (ca. 25 °C).

3.1.2. *Polymerization in toluene*

In order to check whether the use of low polarity solvent can have better control over this polymerization, we performed all the above-mentioned polymerization reactions in a less polar solvent (such as toluene) instead of CH_2Cl_2.

3.1.2.1. Effect of initiator. As mentioned above, in the case of polymerization in CH_2Cl_2, we were unable to study the kinetics because of the fact that this polymerization was almost instantaneous (yield ~100% within 1 min) in presence or in absence of any added salt. However, we try to study the kinetics of this cationic polymerization using our newly developed initiating systems in toluene with the expectation that the rate of polymerization will be much slower compared to that in CH_2Cl_2. Fig. 3A shows the time-conversion profiles of the cationic polymerization of styrene in toluene using

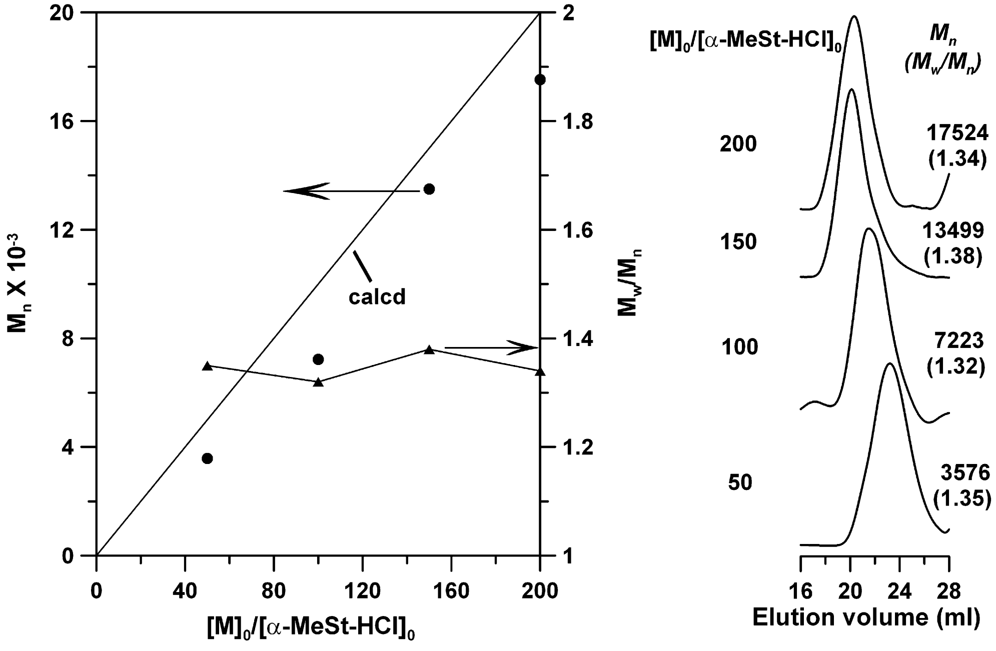


Fig. 1. Plot showing the variation of M_n and PDI with varying initial molar ratio of monomer to III i.e. $[M]_0/[III]_0$ and the corresponding GPC traces of polystyrenes obtained with III/$FeCl_3$/nBu$_4$NI in CH_2Cl_2 at 25 °C: $[M]_0 = 1.0$–4.0 M; $[III]_0 = 20$ mM; $[FeCl_3]_0 = 100$ mM; $[n\text{Bu}_4\text{NI}]_0 = 40$ mM. The line labeled calcd indicates the calculated M_n assuming the formation of one living polymer per adduct (III) molecule.

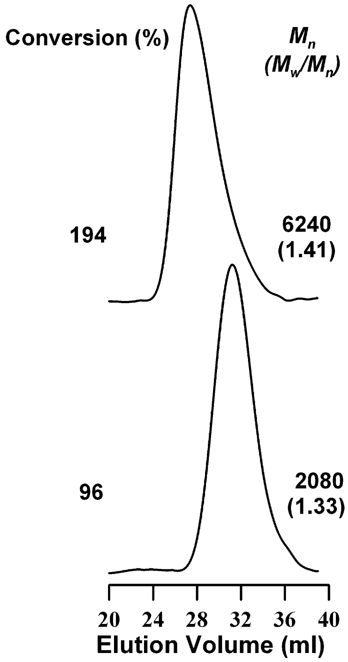


Fig. 2. M_n and PDI of polystyrenes obtained with III/$FeCl_3$/$n$$Bu_4$NI in a monomer-addition experiment in CH_2Cl_2 at 25 °C: $[M]_0 = [M]_{add} = 1.0$ M; $[III]_0 = 20$ mM; $[FeCl_3]_0 = 100$ mM; $[nBu_4NI]_0 = 40$ mM. The molar amount of the second styrene feed was the same as in the first.

(**I**–**III**)/$FeCl_3$/$n$$Bu_4$NBr systems at 25 °C. These results clearly indicate that the rate of polymerization in toluene is indeed much slower compared to that in CH_2Cl_2, although we used same initiating systems. For example, the yield was 72% in 48 h of polymerization in toluene, whereas that was 100% in less than 1 min in CH_2Cl_2. The result also shows that the overall rate of polymerization (R_p) depends on the nature of the initiators and it follows the order: $R_{p,\mathbf{I}} > R_{p,\mathbf{III}} > R_{p,\mathbf{II}}$. The higher reactivity of the C–Br bond compared to that of C–Cl bond might be responsible for such order of propagation rate as also reported elsewhere [49]. Fig. 3B shows the semilogarithmic plot of $\ln\{[M]_0/[M]\}$ vs time of polymerization reactions carried out using **I**, **II** and **III**. Theoretically, for a truly living polymerization system, this semilogarithmic plot should be linear. However, in our case, these plots deviate from linearity for all the three initiators. Usually, the curvature in semilogarithmic plot indicates that the concentration of propagating and reversibly terminated chains decreases more rapidly than the formation of new chains by the slow initiation as in the case of cationic polymerization of styrene with 2-chloro-2,4,4-trimethylpentane/$TiCl_4$/dimethyl acetamide system [48].

Table 1 shows the M_n and MWDs of the polystyrenes thus obtained with (**I**–**III**)/$FeCl_3$ system both in presence and in absence of added salts in toluene. The corresponding GPC traces are shown in Fig. S10 of ESM. According to Table 1, the MWDs of the polystyrenes, obtained with **III** either in presence or in absence of salt, are lower than that obtained using the other two initiators, **I** and **II** (see entries 2–4 and 5–7 in Table 1). From these results, we may consider that **III** is the best initiator among the three initiators used in this polymerization of styrene with $FeCl_3$ in toluene. In the case of polymerization in CH_2Cl_2, we also observed that the **III** is best among all three initiators as mentioned above.

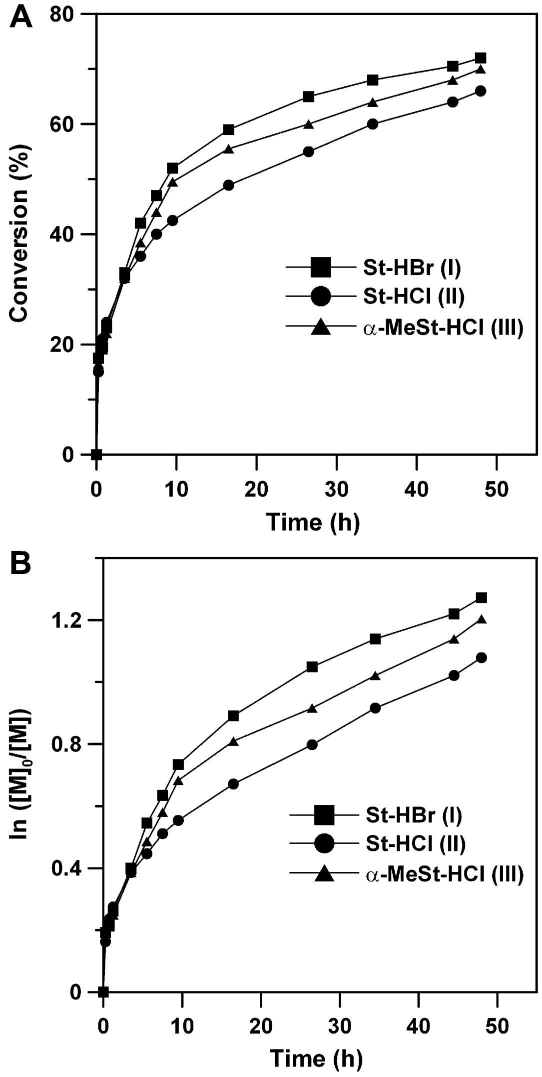


Fig. 3. Time-conversion curves (A) and semilogarithmic plot of monomer concentration vs time (B) for the polymerizations of styrene ($[M]_0 = 1.0$ M) with I or II or III (20 mM)/$FeCl_3$ (100 mM) in presence of $n$$Bu_4$NBr (40 mM) at 25 °C in toluene.

3.1.2.2. Effect of added halide salts (nBu4NY/nR′4PBr). Table 2 shows the M_n and MWDs values of the polystyrenes that were prepared using various tetrabutylammonium halide salts ($nBu_4N^+Y^-$; $Y^- = Br^-, Cl^-, I^-$) and quaternary phosphonium bromide salts (nR'_4PBr; $R' = CH_3CH_2$–, $CH_3(CH_2)_2CH_2$–, $CH_3(CH_2)_6CH_2$–, C_6H_5–). The corresponding GPC traces are shown in Fig. 4. All the GPC traces are unimodal in nature. Note that GPC trace (see 2nd curve of Fig. 4b) of one sample showed one additional peak in the lower molecular weight region. This additional peak arises due to the presence of air in the THF eluent, which are usually coming out after elution of the polymer through the column. In fact, we observed this peak with almost all samples, if we degassed the eluent for long time then its intensity decreases. These peaks are not due to polymers. MWD of the obtained polystyrene without added salt is 1.32, whereas the MWDs of the polystyrenes obtained using added salts such as $n$$Bu_4$NBr, $n$$Bu_4$NCl and $n$$Bu_4$NI are 1.17, 1.05 and 1.08 respectively (compare entry 1 with entries 2–4 in Table 2). It should be noted that MWDs of the polystyrenes obtained using **III**/$FeCl_3$/$n$$Bu_4$NY in toluene are much lower than that obtained using the same initiating systems in CH_2Cl_2 (compare the results of polymerizations in dichloromethane and toluene in Table 2). Also, in our case, the PDIs of the polystyrenes obtained

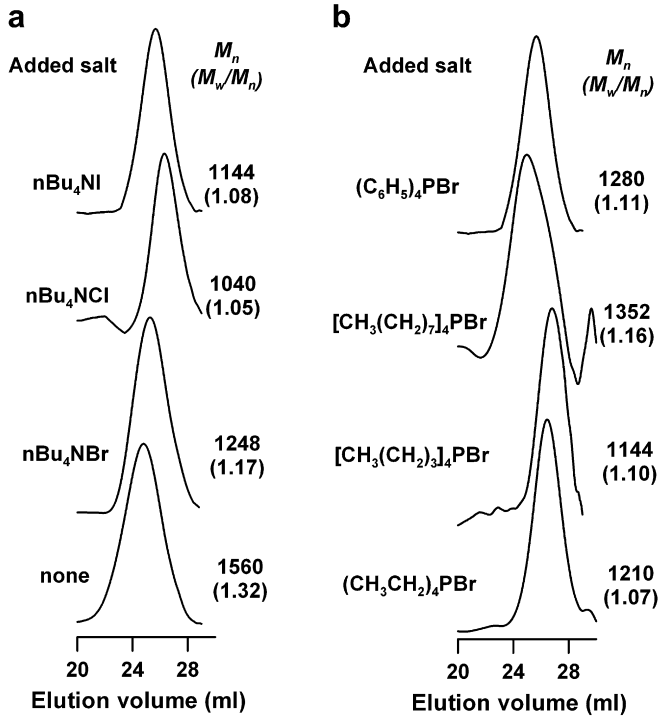


Fig. 4. M_n and PDI of the polystyrenes with their GPC traces ($[M]_0 = 1.0$ M) obtained with III (20 mM)/FeCl$_3$ (100 mM) in presence of added salt (40 mM) at 25 °C in toluene at a conversion of >72%. (a) tetrabutylammonium halide salts; (b) tetraalkylphosphonium bromide salts.

using *n*Bu$_4$NCl and *n*Bu$_4$NI are far less compared to those reported for polystyrenes obtained from cationic polymerization of styrene using other initiating systems [4,5,24,25,27,48,50]. From these results; one may conclude that the polystyrenes with such low PDIs can only be obtained if the polymerization of styrene using **III**/FeCl$_3$/added salt systems behaves like a truly living system. Although, we are unable to make such conclusion from the kinetic study of the same systems in toluene.

We also performed the polymerization of styrene with **III**/FeCl$_3$ in conjunction tetraalkylphosphonium bromide salts instead of quaternary ammonium halides with the expectation that the system would be better controlled. The PDIs of the polystyrenes obtained using tetraalkylphosphonium bromide salts are also low (PDI = 1.07–1.16) as that obtained using tetraalkylammonium halide salts (compare entries 2–4 with entries 5–8 in Table 2). Notably, with increase in the chain length of the alkyl group of quaternary phosphonium bromide salts from C$_2$ to C$_4$ and C$_8$, MWDs of the obtained polystyrenes increases (entries 5–7 in Table 2).

3.1.2.3. Effect of added halide salt concentration. To optimize the reaction condition, polymerization of styrene (1.0 M) with **III**/FeCl$_3$ (20 mM/100 mM) system was carried out at varying concentrations of added salt, *n*Bu$_4$NBr (ca. 0, 20, 40, 60 mM). The M_n and MWD values of the obtained polystyrenes are given in Table 3 (the corresponding GPC traces are shown in Fig. S11 in ESM), which suggested that the polymerization with **III**/FeCl$_3$ system produces polystyrene with narrowest molecular weight distribution at a *n*Bu$_4$NBr concentration of 40 mM (compare entry 3 with entries 1, 2 and 4 in Table 3). This is the reason why we have conducted all the polymerizations at an added salt concentration of 40 mM.

3.1.2.4. Effect of Lewis acid activator (FeCl$_3$) concentration. Four different sets of polymerization reactions (see Table 4) were carried out at styrene/**III**/*n*Bu$_4$NBr = 1000/20/40 mM, but using anhydrous FeCl$_3$ of varying concentrations (ca. 0, 40, 100 and 150 mM) in toluene at 25 °C. M_n and MWD values of the obtained polystyrenes are given in Table 4 (the corresponding GPC traces are shown in Fig. S12 in ESM), which suggested that the polymerization with **III**/*n*Bu$_4$NBr system produces polystyrene with narrowest molecular

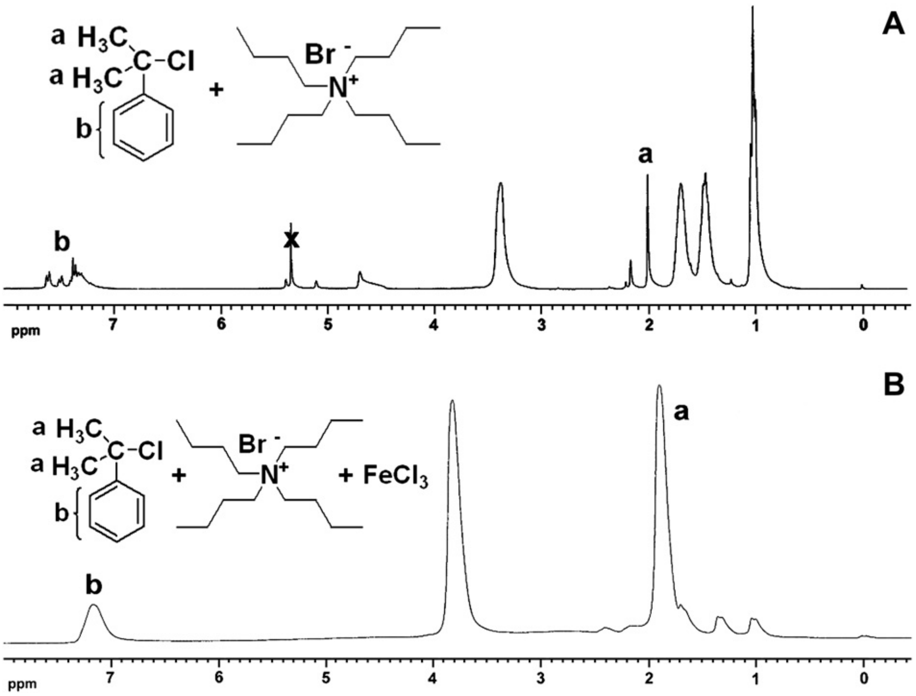


Fig. 5. ^{1}H NMR spectrum of the mixture obtained from the model reaction mimicking the reaction condition of the polymerization reactions involving III and *n*Bu$_4$N$^+$Br$^-$ (A) and involving III, anhydrous FeCl$_3$ and *n*Bu$_4$N$^+$Br$^-$ (B). Polymerization condition: $[\text{III}]_0 = 20$ mM; $[n\text{Bu}_4\text{N}^+\text{Br}^-]_0 = 40$ mM; $[\text{FeCl}_3]_0 = 100$ mM; Temperature = 25 °C; Solvent = CH$_2$Cl$_2$ (the peak X is due to presence of CH$_2$Cl$_2$ in the polymer).

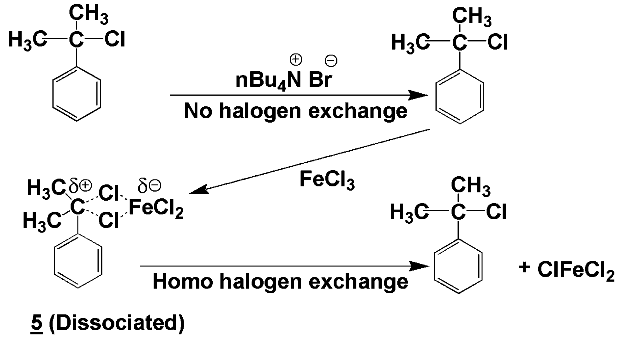
weight distribution only at $FeCl_3$ concentration of 100 mM (compare entries 3 with 2 and 4 in Table 4). This is the reason why we have conducted all the polymerizations at a fixed $FeCl_3$ concentration of 100 mM. Interestingly, we did not observe any polymerization in absence of the Lewis acid activator, $FeCl_3$ (see entry 1 in Table 4).

3.1.2.5. Effect of polymerization temperature. We also conducted polymerization reactions at −25 °C and 0 °C keeping all the other reaction parameters similar to that used at 25 °C to check its effect on the polydispersities of the obtained polymers. Polystyrenes obtained at 25 °C showed narrower MWDs (for GPC traces see Fig. S13 in ESM) compared to that obtained at −25 °C and 0 °C (compare entry 3 with entries 1–2 and entry 6 with entries 4–5 in Table 5). These results indicate that polymerization carried out at lower temperature is poorly controlled than that carried out at 25 °C, provided the other reaction parameters remain unchanged. Similar results were also observed in the case of polymerizations in CH_2Cl_2.

3.1.3. Possible polymerization pathway

To explore a possible polymerization pathway for this polymerization of styrene using **III**/$FeCl_3$ system in presence of added salts, first of all, we carried out some model reactions. We then analyzed these reactions via ^1H NMR spectroscopy. The model reactions are the actual polymerization reactions, but were carried out in absence of monomer (here, styrene). The reaction recipes were as follows: HX-adduct (**I** or **III**) 20 mM; $FeCl_3$ 100 mM; added salt 40 mM.

The first model reaction was the reaction of **III** with a solution of $nBu_4N^+Br^-$. We acquired the ^1H NMR spectrum of this reaction mixture (see Fig. 5A). But, we did not observe any change of the characteristic peaks of **III** in the mixture in comparison to that of neat **III**. The result indicates that there is no structural change of **III** due to this reaction, i.e. there is no halogen exchange between **III** and $nBu_4N^+Br^-$. However, the ^1H NMR spectrum of the mixture after adding anhydrous $FeCl_3$ shows a clear shift in the signals of the methyl protons of **III** from δ 1.99 ppm to δ 1.86 ppm (compare Fig. 5A with Fig. 5B). Such shift is probably due to the generation of a new dissociated species 5 in the mixture by the dynamic halogen exchange between chlorine atom of $FeCl_3$ with that of **III** (see Scheme 3).



Scheme 3. Possible homohalogen exchange pathway of the model reaction using HX-styrenic monomer adduct/FeCl3 in the presence of added salt.

Similar experiments were also conducted with initiator **I** and nBu_4N^+I, but we did not observe any halogen exchange via ^1H NMR

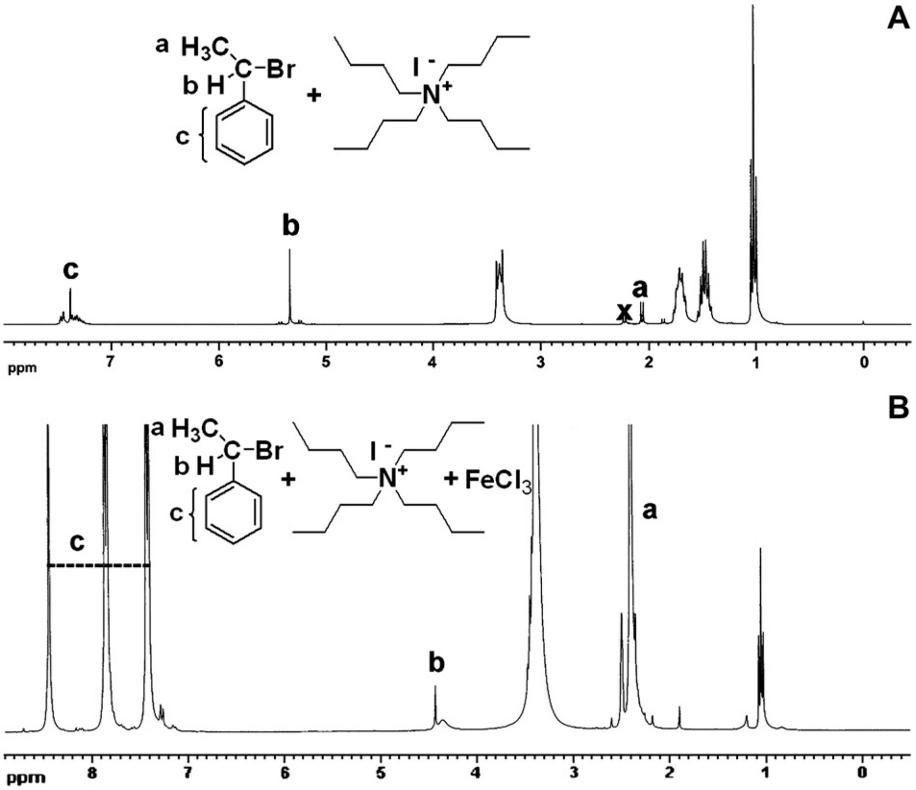
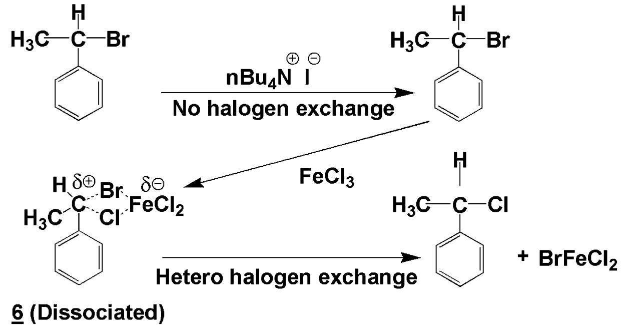


Fig. 6. ^1H NMR spectrum of the mixture obtained from the model reaction mimicking the reaction condition of the polymerization reactions involving I and $nBu_4N^+I^-$ (A) and involving I, anhydrous $FeCl_3$ and $nBu_4N^+I^-$ (B). Polymerization condition: $[I]_0 = 20$ mM; $[nBu_4N^+I^-]_0 = 40$ mM; $[FeCl_3]_0 = 100$ mM; Temperature = 25 °C; Solvent = CH_2Cl_2. (the peak X is an unidentified peak).



Scheme 4. Possible heterohalogen exchange pathway of the model reaction using HX-styrenic monomer adduct/FeCl3 in the presence of added salt.

spectroscopy (see Fig. 6A). When anhydrous $FeCl_3$ was added to this mixture, the ^{1}H NMR spectrum of the mixture exhibits a shift of the characteristic methine and methyl signals (CH/CH_3; δ, ppm) from δ 5.32/2.03 ppm to δ 4.42/2.40 ppm (Fig. 6B). In this case, this shift is probably due to the rapid conversion of PhCH(Br) to PhCH(Cl) via a dissociated species 6 by the dynamic halogen exchange between the chlorine atom of $FeCl_3$ with the bromine atom of adduct, **I** (see Scheme 4).

Therefore, from these NMR results, we may conclude that there is a rapid halogen exchange between the growing end and the $FeCl_3$ (activator) no matter whether the reaction is initiated either with the alkyl chloride (ca. **III**) or the alkyl bromide (ca. **I**). Also, as there is no dissociated species (see 5 or 6 in Schemes 3,4) formation in absence of $FeCl_3$, one should not expect any polymerization upon addition of styrene to this system. Indeed, we did not obtain any polymer in absence of $FeCl_3$ (entry 1 in Table 4) as mentioned above. Similar halogen exchange reactions have also been studied earlier to propose the possible mechanistic pathway for their polymerization system [25,51].

To ascertain the possible mechanism, it is also necessary to know the end group of the polystyrene, obtained from the polymerization of styrene with **III**/$FeCl_3$/added salt system. Thus, ^{1}H NMR spectroscopic characterization was performed on some of the representative polystyrene samples. ^{1}H NMR spectrum (Fig. 7) of one of such samples shows a broad signal around δ 3.48 ppm that can be assigned to the methine proton of the halide terminal [$-CH_2CH(Ph)-Y$]. Peaks for the $-CH_3$ protons of the polystyrene were observed at δ 1.03 ppm. All other characteristic of polystyrene comes at their respective positions [42]. The spectra of other samples also exhibit similar broad signal at around 3.48 ppm, irrespective of the conversion and the types of the halogens X and Y in the initiator and in the added halide salt. These spectra are not shown here for brevity. Similar results were also observed by other researchers for their system [42]. In general, living cationic polymerizations of styrene/vinyl monomers are terminated by adding prechilled methanol containing a little amount of NH_3 (0.1%). Therefore, the polymers obtained via such kind of polymerization/termination usually have four possible end groups (see Scheme 5). These are: (i) a methoxide ($-OCH_3$) end group formed by the covalent attachment of $-OCH_3$ to the propagating carbocationic end [43], (ii) halogen atom as the end group [6,42,44,48], (iii) an olefinic end group formed by the chain termination reaction through β-hydrogen elimination reaction [52] and (iv) an indanyl ring as the end group [4,12,40]. However, no other characteristic peaks were observed for other possible end groups such as an indan or an olefin or a methoxide (though the polymerization was quenched with methanol).

The absence of the terminal methoxide group indicated a strong interaction between the terminal carbon and halogen. The living nature of this polymerization of styrene by (**I**–**III**)/$FeCl_3$/added salt system was justified by the absence of the indan and the olefinic terminals as the end group of the polystyrene chain. This polymerization of styrene using $FeCl_3$ is free from chain transfer and chain termination reactions, because if that be the case, indanic or olefinic end group would be present, instead of halide as the end group.

From the above-mentioned polymerization results, we observed that the polymerization of styrene at room temperature (25 °C) is better controlled only in presence of all the three components of the initiating system i.e. HX-adduct, $FeCl_3$ and the added salt. Also, end group analysis of the obtained polystyrene shows the presence of halogen atom at the end. Based on these results as well as the study of the model reactions, herein we propose the following reaction sequence (see Scheme 6) as a possible pathway for this polymerization of styrene initiated with the HX-adduct/$FeCl_3$/added salt system. At first, the metal halide ($FeCl_3$) activates the C–X bond of the initiator and generates a dissociated species, which interacted with styrene through its carbocationic center and starts the propagation. The role of the counteranion (Y^-) of the added salt is to stabilize the propagating end of the carbocationic species and thus to induce livingness to the polymerization system. The cationic part of the added salt of AY i.e. A^+ has a role to play for this substitution process. It actually forms an ion pair with $[FeCl_3X]^-$ and thus provides a driving force for the substitution of X by Y and this substitution facilitates the propagation of the polymerization. The above-mentioned result of the end group analysis clearly showed the presence of counteranion (Y^-) at the end of the polystyrene chain.

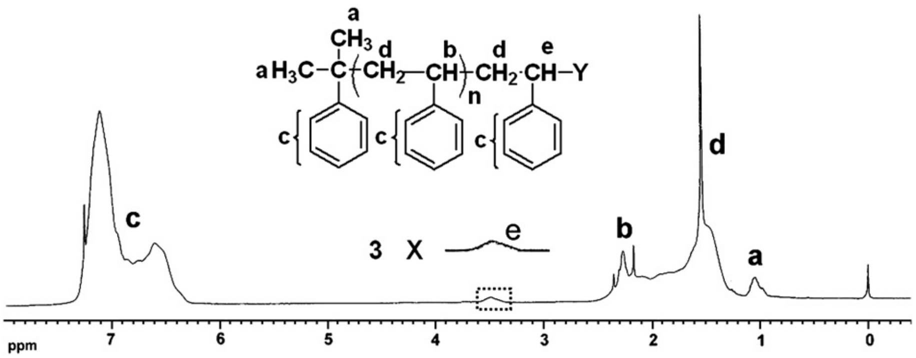
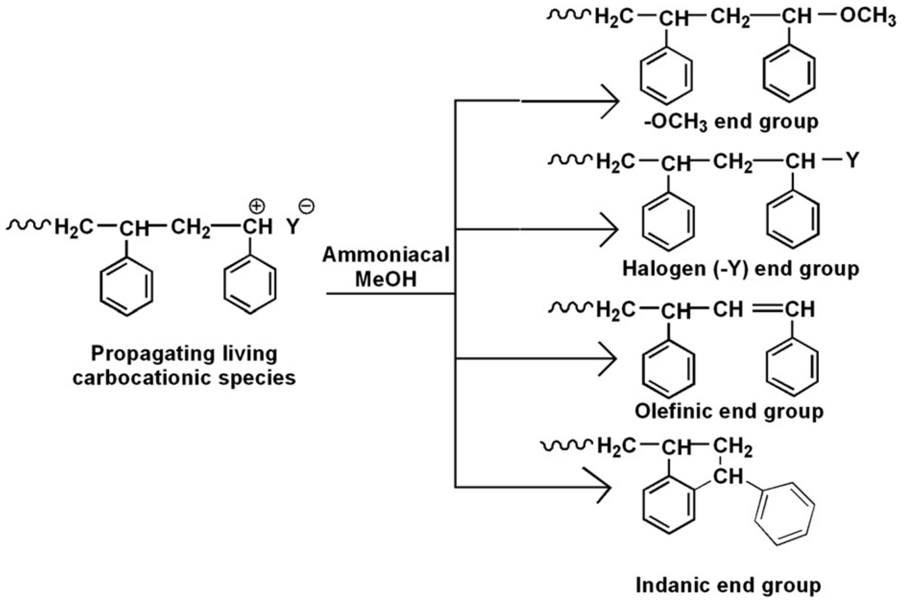
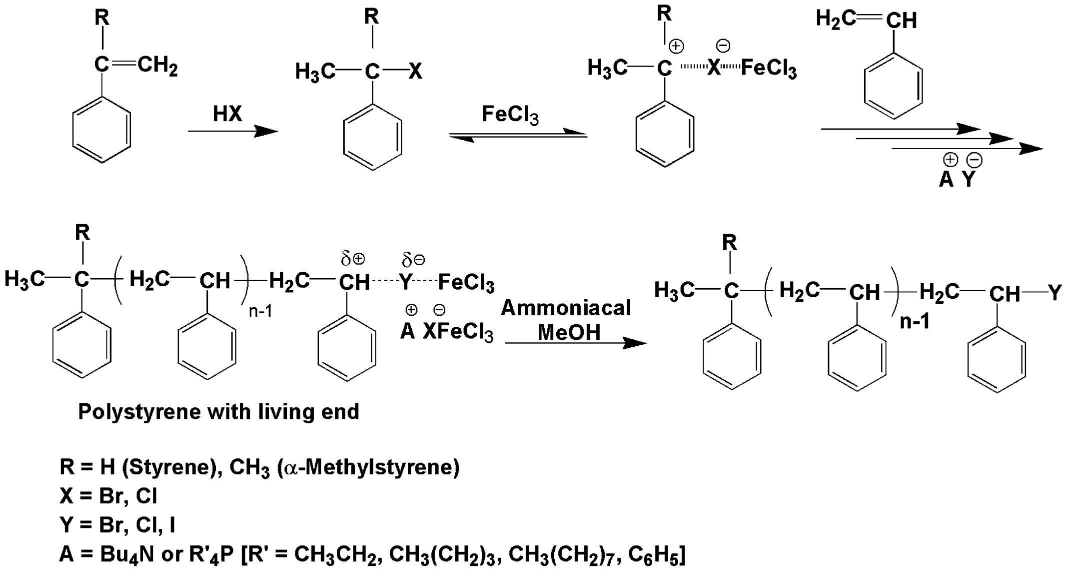


Fig. 7. ^{1}H NMR spectrum of polystyrene obtained with III/$FeCl_3$/nBu$_4$NI in CH_2Cl_2 at 25 °C after quenching the polymerization with ammonical methanol at a monomer conversion of >90%. Polymerization condition: $[M]_0 = 1.0$ M; $[III]_0 = 20$ mM; $[FeCl_3]_0 = 100$ mM; $[nBu_4NI]_0 = 40$ mM.



Scheme 5. Chemical structures of four possible end groups attached to polystyrene chains.



Scheme 6. Possible polymerization pathway of living cationic polymerization of styrene using FeCl3 in presence of added salt.

4. Conclusions

In summary, we have systematically investigated the cationic polymerization of styrene using a newly designed initiating systems consisting of HX-styrenic monomer adduct (see **I–III** in Scheme 1)/$FeCl_3$ system in presence of added halide salts. A particular advantage of this initiating system over those reported previously is that it enables the synthesis of well-defined living polystyrenes even at room temperature (ca. 25 °C). The polymerization was poorly controlled in absence of the added halide salt. That is the use of the added salt (tetrabutylammonium halide or tetraalkylphosphonium bromide or tetraphenylphosphonium bromide) was mandatory to achieve controlled living polymerization. The appropriate combination of the concentrations of the components of the $FeCl_3$ based initiating system, polarity of the solvent used for the polymerization, and polymerization temperature were needed to obtain polystyrene with narrow molecular weight distribution. The polymerization was instantaneous (within 1 min) and quantitative (yield ~100%) in CH_2Cl_2. Living nature of this polymerization in CH_2Cl_2 was confirmed by the successful monomer addition experiment as well as from the study of molecular weights of obtained polystyrenes prepared simply by varying monomer to initiator ratio. The polymerization in CH_2Cl_2 produces polystyrenes with polydispersities ranging from 1.33 to 1.38. But, the polystyrene obtained from toluene showed extremely narrow PDIs (1.05–1.17). A possible polymerization pathway was suggested based on the results of the ^{1}H NMR spectroscopic analysis of the model reactions as well as the end group analysis of the obtained polymers.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.01.051.

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