Living Carbocationic Polymerization of *p*-Methoxystyrene Using *p*-Methoxystyrene Hydrochloride/SnBr$_4$ Initiating System: Determination of the Absolute Rate Constant of Propagation for Ion Pairs

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ABSTRACT: The carbocationic polymerization of *p*-methoxystyrene (*p*-MeOSt) was studied in CH$_2$Cl$_2$ at −30 °C using 1-chloro-1-(*p*-methoxyphenyl)ethane (*p*-MeOStCl) as initiator in conjunction with different Lewis acids, $BF_3 \cdot O(C_2H_5)_2$, BCl$_3$, ZnCl$_2$, TiCl$_4$, SnCl$_4$, and SnBr$_4$. The best results, moderate rates, theoretical M_ns, and low polydispersities, were obtained in conjunction of SnBr$_4$. The living nature of the polymerization was verified by linear first-order $\ln([M]_0/[M])$ vs time and linear M_n vs conversion plots in the temperature range of −60 to −20 °C. The number-average molecular weight of the polymers increased in direct proportion to monomer conversion up to $M_n = 120\,000$ and agreed with the calculated molecular weight, assuming that one polymer chain forms per molecule of *p*-MeOStCl. Kinetic studies suggest that the polymerization is first order in [SnBr$_4$], and the rate, M_n, and polydispersity index are not affected by excess proton trap, 2,6-di-*tert*-butylpyridine. The living nature of the polymerization was further demonstrated by chain extension experiment. The stability of the propagating chain end of poly(*p*-MeOSt) and monomeric chain end of *p*-MeOSt$^+$ was studied, and a slow decomposition of the active chain end was observed under monomer starved conditions. Employing the model compound *p*-MeOStCl in conjunction with SnBr$_4$ in CH$_2$Cl$_2$ UV−vis spectroscopy was used to determine the equilibrium constant of ionization (K_i) at −30 and −60 °C. From K_i values and the apparent rate constant of propagation (k_{app}), the absolute rate constant of propagation for ion pairs, $k_p^{\pm} = 1.07 \times 10^5$ L mol^{-1} s^{-1} for −30 °C and 3.83×10^4 L mol^{-1} s^{-1} for −60 °C, was calculated. To determine $k_p^{\pm}$ separately, competition experiments were carried out in the presence of a nucleophile, phenylsilane. NMR spectroscopy, gel permeation chromatography, and MALDI−TOF MS analysis suggested complete capping of the polymeric cation and the absence of side reactions. From the limiting conversion and limiting number-average degree of polymerization $k_p^{\pm}$ was calculated using the known rate constant of capping. The $k_p^{\pm}$ values obtained from the competition experiments agreed well with those determined from the UV−vis spectroscopy.

Introduction

The absolute rate constant of propagation for ion pairs ($k_p^{\pm}$) in the cationic homopolymerization of isobutylene (IB)[1] and styrene (St)[2] was recently determined by the diffusion clock method. For both IB and St, the $k_p^{\pm}$ values were in good agreement with those predicted by the linear free energy relationship (LFER) by Mayr;[3] however, they were 4−6 orders of magnitude higher than previously accepted values.[4] We are extending our work to St derivatives and have recently reported preliminary results for 2,4,6-trimethylstyrene (TMeSt), where both UV spectroscopy and competition experiments at −70 °C yielded similar $k_p^{\pm} \sim (1-3) \times 10^4$ L mol^{-1} s^{-1}.[5] The present study focuses on *p*-methoxystyrene (*p*-MeOSt). The living cationic polymerization of *p*-MeOSt was first reported with the HI/ZnI$_2$ initiating system in toluene at −15 to 25 °C.[6] Living polymerizations were also attained in the more polar solvent, CH$_2$Cl$_2$, with the HI/I$_2$ and HI/ZnI$_2$ initiating systems in the presence of tetra-*n*-butylammonium salts (*n*Bu$_4$NX; X = Cl, Br, I).[7] Comparable but less controlled polymerization of *p*-MeOSt has been reported using iodine as an initiator in carbon tetrachloride.[8] This system gives rise to long-lived but not truly living polymerization. A recent report indicated the controlled cationic polymerization of *p*-MeOSt with controlled molecular weights and relatively narrow molecular weight distribution (PDI = 1.4) using the *p*-MeOSt−HCl adduct (*p*-MeOStCl)/Yb(OTf)$_3$ initiating system in the presence of 2,6-di-*tert*-butyl-4-methylpyridine.[9] The authors also claimed the controlled cationic polymerization of *p*-MeOSt with very slow polymerization in aqueous media using the *p*-MeOStCl/Yb(OTf)$_3$ initiating system. Relatively narrow PDI (∼1.4) were observed, and the molecular weights increased in proportion to the monomer conversion. More recently, surfactants,[10] sulfonic acid-based initiators,[11] and various phosphonic acid initiators[12] were used for the cationic polymerization of *p*-MeOSt in aqueous medium. Weak Lewis acids such as SnBr$_4$ have not been used as co-initiators to study the living cationic polymerization of *p*-MeOSt.

For the cationic polymerization of *p*-MeOSt using both calorimetry and spectrophotometry, Cotrel et al. reported $k_p = 7.4 \times 10^4$ and 1.4×10^4 L mol^{-1} s^{-1} at −15 and 10 °C, respectively.[13] Stopped-flow/rapid-scanning spectroscopy was also applied to study the polymerization of *p*-MeOSt in CH$_2$Cl$_2$ and in mixed solvents by numerous initiators, and considering the absorption of the propagating cation at 380 nm, k_p values ranging from 4×10^3 to 1.3×10^5 L mol^{-1} s^{-1} have been reported.[14] As pointed out by Plesch,[4] however, assignment of the 380 nm peak for the *p*-MeOSt cation is erroneous. Recently, using laser flash photolysis, McClelland et al.[15] have shown that λ_{max} for the *p*-MeOSt cation is at 340 nm, which was earlier given by De Sorgo et al.[16]

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In this study, the polymerization of *p*-MeOSt initiated by *p*-MeOStCl, a model propagating chain end, was studied in CH_2Cl_2 at −20 to −60 °C using $SnBr_4$, a weak Lewis acid. UV−vis spectroscopy and competition experiments have been carried out to determine $k_p^{\pm}$ separately.

Experimental Section

Materials. The *p*-methoxystyrene (*p*-MeOSt, Aldrich, 97%) was distilled from calcium hydride (CaH_2) under reduced pressure and stored under nitrogen at −20 °C, and just before use it was again distilled from CaH_2 under reduced pressure. The 1-chloro-1-(*p*-methoxyphenyl)ethane (*p*-MeOStCl) was synthesized just before use by bubbling dry HCl gas into *p*-MeOSt in CH_2Cl_2 (1:10 *p*-MeOSt/CH_2Cl_2 (v/v)) under stirring at −78 °C, and then dry nitrogen was bubbled to remove excess HCl. Finally, CH_2Cl_2 was removed using a vacuum pump. ^{1}H NMR spectrum: *p*-MeOStCl; 7.41 (d), 6.94 (d), 5.1−5.2 (q), 3.86 (s), and 1.89 ppm (d). The CH_2Cl_2 was shaken with 5% NaOH and then repeatedly with water. Then it was predried with anhydrous Na_2SO_4 and distilled from CaH_2 under nitrogen. This distilled CH_2Cl_2 was refluxed under nitrogen overnight with P_2O_5 and distilled to a round-bottom flask over P_2O_5. It was refluxed under nitrogen overnight and distilled just before use. Phenylsilane (97%, Aldrich), $SnBr_4$ (99%, Aldrich), and 2,6-di-*tert*-butylpyridine (DTBP, 97%, Aldrich) were used as received. All other chemicals and solvents were purified as described previously or used as received.[1]

Polymerization. Polymerizations were carried out under a dry nitrogen atmosphere ($[H_2O] < 0.5$ ppm) in an MBraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). Large (75 mL) culture tubes were used as polymerization reactors. The total volume of the reaction mixture was 15 mL. After predetermined time polymerization was terminated by the addition of 0.5 mL of prechilled methanol. The polymer was recovered and purified two times by reprecipitation from CH_2Cl_2/methanol. Monomer conversions were determined by gravimetric analysis.

Competition experiments were carried out in the presence of phenylsilane as a capping agent. In a typical competition experiment the polymerization was carried out in CH_2Cl_2 at −30 °C using the following concentration: [*p*-MeOStCl] = 0.001 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [*p*-MeOSt] = 0.15 mol L^{-1}, [$TiCl_4$] = 0.003 mol L^{-1}, [phenylsilane] = 0.75 mol L^{-1}. Into a 75 mL culture tube at −30 °C 12.1 mL of CH_2Cl_2 at room temperature, 0.45 mL of DTBP stock solution in CH_2Cl_2 (0.2 mol L^{-1}) at −30 °C, 0.31 mL of *p*-MeOStCl stock solution in CH_2Cl_2 (0.045 mol L^{-1}) at −30 °C, 1.0 mL of *p*-MeOSt stock solution in CH_2Cl_2 (2.25 mol L^{-1}) at −30 °C, and 1.4 mL of phenylsilane at room temperature were added and mixed thoroughly. The polymerization was started by the addition of 0.47 mL of $TiCl_4$ solution (0.09 mol L^{-1}, in CH_2Cl_2) at −30 °C. After a predetermined time (15 min) 0.5 mL of prechilled methanol was added to the reaction mixture to quench the polymerization. The polymer was precipitated twice from CH_2Cl_2/methanol to obtain 107 mg of polymer (conversion = 35.3%, $M_{n,GPC}$ = 7400, PDI = 2.7).

Characterization. Molecular weights were measured using a Waters HPLC system equipped with a model 510 HPLC pump, a model 250 dual refractometer/viscometer detector (Viscotek), a model 486 UV/vis detector, a model 712 sample processor, and five ultra-Styragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL/min at room temperature. The measurements were carried out at room temperature. The number-average molecular weights (M_n) and polydispersities (PDI) were determined using the conventional calibration curve and Viscotek TriSEC GPC software. Molecular weights were also calculated by the universal calibration obtained by polystyrene standards; however, the M_n values were very similar to that obtained from conventional calibration using polystyrene standards. The ^{1}H NMR spectroscopy was carried out on a Bruker 250 MHz spectrometer using $CDCl_3$ as a solvent (Cambridge Isotope Lab., Inc.). ^{1}H NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane as internal standard (δ_H 0.00).

MALDI−TOF MS. The MALDI-MS and post source decay (PSD) MALDI-MS/MS measurements were performed with a Bruker BIFLEX III mass spectrometer equipped with a time-of-flight (TOF) analyzer. In all cases 19 kV acceleration voltage was used with pulsed ion extraction (PIE). The positive ions were detected both in the reflectron mode (20 kV) and in the linear mode. A nitrogen laser (337 nm, 3 ns pulse width, 10^6−10^7 W/cm^2) operating at 4 Hz was used to produce laser desorption.

The samples (5 mg/mL) in THF were prepared with a dithranol matrix (20 mg/mL in THF). To produce silver cationized peaks, silver trifluoroacetate (AgTFA) dissolved in THF at a concentration of 1 mg/mL was added to the matrix/analyte solution. The solutions were mixed in 10:2:1 v:v ratio (matrix:analyte:AgTFA). A volume of 0.5 μL of these solutions was deposited onto the sample plate (stainless steel) and allowed to air-dry.

UV−Vis Spectroscopy. UV−vis spectroscopic measurements were carried out under a dry nitrogen atmosphere in the glovebox. A quartz immersion probe (661.300-QX, Hellma, optical path: 0.5 or 0.02 cm) connected to a fiber-optic visible (tungsten light source, Ocean Optics) and UV (AIS model UV-2, Analytical Instrument Systems, Inc.) light source and a Zeiss MMS 256 photodiode array detector was used. The latter was connected to a personal computer via a TEC5 interface, and the spectra were recorded using the “Aspect Plus” software (Zeiss).

Table 1. Results for the Cationic Polymerization of *p*-MeOSt Using Different Lewis Acid/*p*-MeOStCl Initiating System in CH_2Cl_2 at −30 °C[a]

expt	Lewis acid	[Lewis acid] (mol L^{-1})	time (min)	conv (%)	M_n	PDI
1	$BF_3.O(C_2H_5)_2$	0.02	42	66.7	267 300	1.8
2	$BF_3.O(C_2H_5)_2$	0.07	10	98.2	221 000	2.1
3	BCl_3	0.003	5	98.2	19 000	1.7
4	BCl_3	0.006	5	100	20 600	1.6
5	BCl_3	0.012	5	100	16 500	2.1
6	$ZnCl_2$	0.003	30	17.2	5 400	2.7
7	$ZnCl_2$	0.009	30	56.2	12 100	1.1
8	$ZnCl_2$	0.016	30	94.5	19 100	1.3
9	$TiCl_4$	0.0035	1	100	21 400	1.7
10	$TiCl_4$	0.006	1	100	18 400	1.9
11	$SnCl_4$	0.0035	0.5	97.6	21 000	1.4
12	$SnCl_4$	0.01	1	100	22 400	1.7
13	$SnBr_4$	0.004	5	68.9	14 300	1.05
14	$SnBr_4$	0.008	3	72.5	15 600	1.04
15	$SnBr_4$	0.025	5	100	22 600	1.05

[a] [DTBP] = 0.004 mol L^{-1}, [*p*-MeOSt] = 0.15 mol L^{-1}, and [*p*-MeOStCl] = 0.001 mol L^{-1}.

Results and Discussion

Living Cationic Polymerization of *p*-MeOSt. Search for Lewis Acid Coinitiator. The cationic polymerization of *p*-MeOSt was carried out using *p*-MeOStCl as initiator (0.001 mol L^{-1}) in the presence of DTBP (0.004 mol L^{-1}) as proton trap in CH_2Cl_2 at −30 °C using $BF_3.O(C_2H_5)_2$, BCl_3, $ZnCl_2$, $TiCl_4$, $SnCl_4$, and $SnBr_4$ as Lewis acids. The results are presented in Table 1. The cationic polymerization of *p*-MeOSt using $BF_3 \cdot O(C_2H_5)_2$ as coinitiator is uncontrolled and yields polymers with M_ns much higher than the theoretical value and broad molecular weight distribution. Using BCl_3, theoretical molecular weights but high polydispersities were obtained since the polymerization was too fast. Polymerization with $ZnCl_2$ (in diethyl ether) in the concentration range 0.01−0.02 mol L^{-1} gives poly(*p*-MeOSt) with theoretical molecular weight. The molecular weight distribution decreases to 1.1 at 60−80%

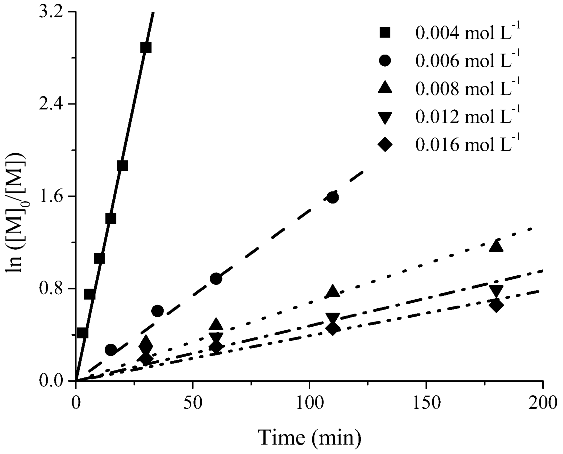


Figure 1. Polymerization of *p*-MeOSt initiated with *p*-MeOStCl/$ZnCl_2$ in the presence of increasing concentration of DTBP at −30 °C in CH_2Cl_2; [*p*-MeOSt] = 0.15 mol L^{-1}, [*p*-MeOStCl] = 0.001 mol L^{-1}, and [$ZnCl_2$] = 0.016 mol L^{-1}.

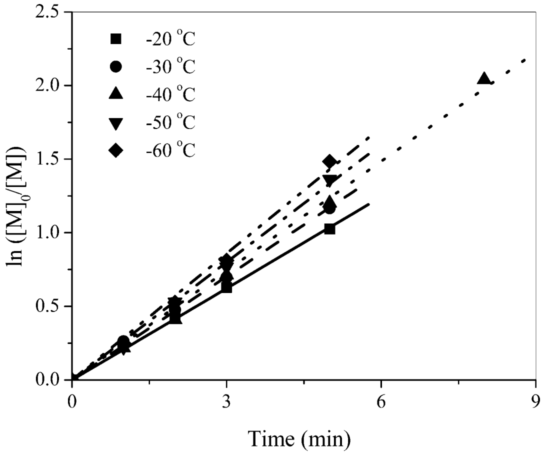


Figure 2. First-order plot of ln([M]$_0$/[M]) vs time for the cationic polymerization of *p*-MeOSt initiated by *p*-MeOStCl/$SnBr_4$ in CH_2Cl_2; [*p*-MeOStCl] = 0.001 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [*p*-MeOSt] = 0.15 mol L^{-1}, [$SnBr_4$] = 0.004 mol L^{-1}.

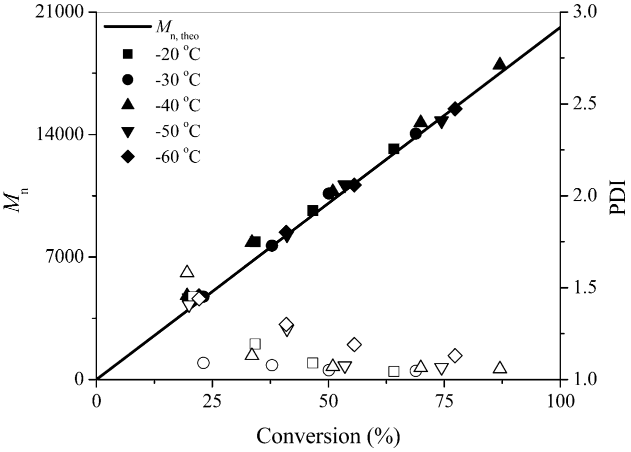


Figure 3. Variation of M_n and PDI with conversion. Reaction conditions are the same as in Figure 2.

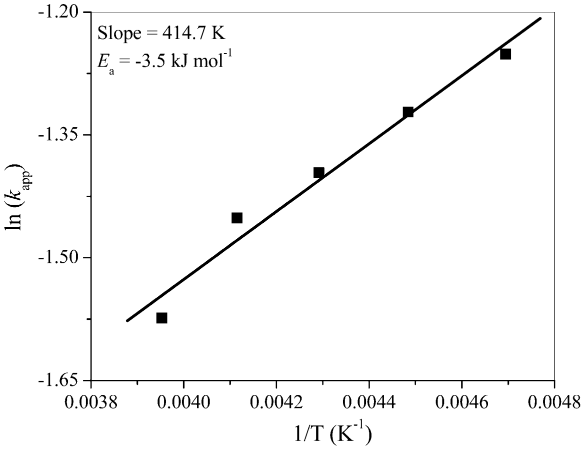


Figure 4. Arrhenius plot of ln(k_{app}) vs 1/*T* to determine apparent energy of activation, E_a, for the cationic polymerization of *p*-MeOSt initiated by *p*-MeOStCl/$SnBr_4$ in CH_2Cl_2; [*p*-MeOStCl] = 0.001 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [*p*-MeOSt] = 0.15 mol L^{-1}, [$SnBr_4$] = 0.004 mol L^{-1}.

conversion and then increases to 1.2−1.3 at 100% conversion. Sequential monomer addition experiments (not shown), however, proved the nonliving nature of the polymerization. As shown in Figure 1, the polymerization rate decreases with increasing DTBP concentration, suggesting a complex nature of the polymerization with possible complexation between $ZnCl_2$ and DTBP. Cationic polymerization of *p*-MeOSt using the *p*-MeOStCl/$TiCl_4$ initiating system gives poly(*p*-MeOSt) with theoretical molecular weight, but because of the extremely rapid polymerization, the molecular weight distribution is broad. The theoretical molecular weight was also obtained with PDI = 1.4−1.7 using $SnCl_4$, but again the polymerization is extremely rapid. Importantly, the polymerization induced by $SnBr_4$ proceeds with a moderate rate, and the polymers exhibited narrow molecular weight distribution (PDI < 1.1). On the basis of these results, we have selected the *p*-MeOStCl/$SnBr_4$ initiating system in CH_2Cl_2 at −30 °C to study the living cationic polymerization of *p*-MeOSt in detail.

Effect of Temperature. The cationic polymerization of *p*-MeOSt with $SnBr_4$ was carried out at different temperatures. At all temperatures, the first-order plots of ln([M]$_0$/[M]) vs time were linear starting at the origin (Figure 2), and the slope of this plot was calculated to determine the apparent rate constant of propagation (k_{app}). The linear first-order plots obtained at all temperatures indicate the absence of irreversible termination during the polymerization. The number-average molecular weight (M_n) and the polydispersity index (PDI = M_w/M_n) vs conversion plots are shown in Figure 3. The molecular weights of the poly(*p*-MeOSt) are directly proportional to the conversion and follow the theoretical M_n−conversion line at all temperatures, indicating the absence of chain transfer during the polymerization. For polymerizations at all temperatures the PDI decreases with increasing conversion and reaches well below 1.1 after ~60% conversion. The linear M_n−conversion plots together with the linear first-order plots indicate that the polymerization of *p*-MeOSt is living in the studied temperature range.

The apparent rate constant of propagation, k_{app}, increases with decreasing temperature. The apparent activation energy of polymerization, $E_a = -3.5$ kJ mol^{-1}, was calculated from the Arrhenius plot of ln(k_{app}) vs 1/*T* (Figure 4). It is noteworthy to mention that negative E_a has already been reported for the cationic polymerization of various monomers such as St,[2] IB,[17] α-methylstyrene,[18] TMeSt,[5] and indene.[19] The negative E_a has been attributed to the decrease of the extent of chain end ionization with increasing temperature.

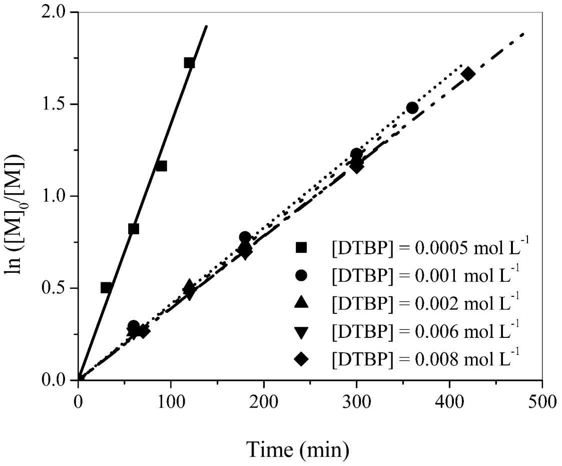


Figure 5. Polymerization of *p*-MeOSt initiated with *p*-MeOStCl/$SnBr_4$ in the presence of increasing concentration of DTBP at −30 °C in CH_2Cl_2; [*p*-MeOSt] = 0.15 mol L^{-1}, [*p*-MeOStCl] = 0.001 mol L^{-1}, and [$SnBr_4$] = 0.004 mol L^{-1}.

Control experiments (direct initiation) were also carried out in the absence of initiator. Under the same conditions, 5.5%, 11.3%, 15.1%, and 23.1% monomer conversions were obtained after 5, 11, 17, and 30 min, respectively. This confirms that direct initiation is operational during the cationic polymerization of *p*-MeOSt initiated by *p*-MeOStCl/$SnBr_4$, but it is much slower than in the presence of initiator, *p*-MeOStCl, and the kinetics of polymerization is unaffected.

Effect of DTBP. The DTBP, a hindered pyridine, is generally used in the carbocationic living polymerization to prevent protic initiation.[20] Thus, we have studied the polymerization of *p*-MeOSt in the presence and absence of DTBP with the *p*-MeOStCl/$SnBr_4$ initiating system in CH_2Cl_2 at −30 °C. In absence of DTBP 100% conversion was reached in less than 1 min. The molecular weight was higher than the expected theoretical molecular weight (M_n = 25 400, PDI = 1.8[21] vs theoretical M_n, $M_{n,theo}$ = 20 100). When the polymerization experiments were carried out in the presence of DTBP, the difference from the theoretical molecular weight decreased with increasing DTBP concentration. The polymerization rates also decreased as [DTBP] increased from 0.0005 to 0.001 mol L^{-1}; however, above this value the polymerization rate remained unchanged as shown in Figure 5. At [DTBP] = 0.001 mol L^{-1}, close to theoretical molecular weights and very narrow molecular weight distributions are observed (Figure 6), as apparently all protic impurities have been scavenged. Above [DTBP] = 0.001 mol L^{-1} the polymerization rates, M_ns, and PDIs are independent of DTBP concentration; thus, the polymerization is unaffected by excess DTBP. So in all further experiments [DTBP] = 0.006 mol L^{-1} was used in the polymerization.

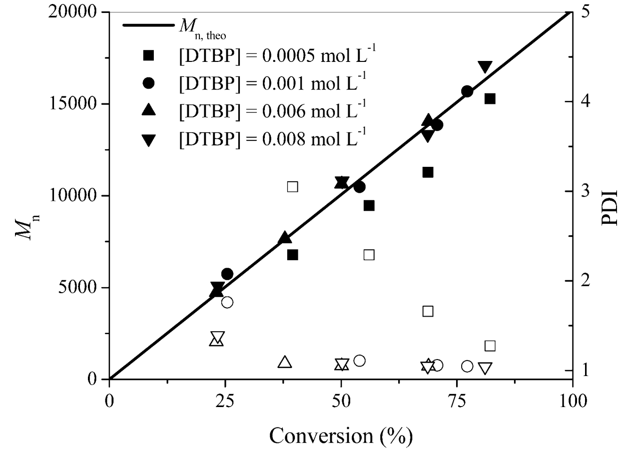


Figure 6. M_n and PDI of the polymers obtained from the polymerization of *p*-MeOSt initiated with *p*-MeOStCl/$SnBr_4$ in the presence of increasing concentration of DTBP at −30 °C in CH_2Cl_2; [*p*-MeOSt] = 0.15 mol L^{-1}, [*p*-MeOStCl] = 0.001 mol L^{-1}, and [$SnBr_4$] = 0.004 mol L^{-1}: (solid symbols) M_n; (open symbols) PDI; straight line indicates the M_n assuming that one polymer chain forms per molecule of *p*-MeOStCl.

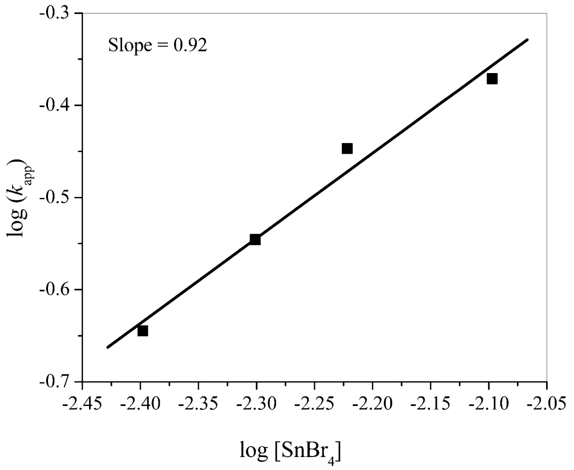


Figure 7. Plot of log(k_{app}) vs log([$SnBr_4$]) in the polymerization of *p*-MeOSt in CH_2Cl_2 solvent at −30 °C; [*p*-MeOSt] = 0.15 mol L^{-1}, [*p*-MeOStCl] = 0.001 mol L^{-1}, and [DTBP] = 0.006 mol L^{-1} at [$SnBr_4$] = 0.004−0.008 mol L^{-1}.

Dependence of Polymerization Rate on [$SnBr_4$]. The reaction order in [$SnBr_4$] was investigated for the polymerization of *p*-MeOSt in CH_2Cl_2 at −30 °C. First-order plots were constructed for the polymerization of *p*-MeOSt using the *p*-MeOStCl/$SnBr_4$ initiating system in CH_2Cl_2 at −30 °C at four different concentrations of $SnBr_4$ (0.004−0.008 mol L^{-1}). As expected, the rate of polymerization increases with increasing concentration of $SnBr_4$. The first-order plots were linear at all $SnBr_4$ concentrations. The M_n of the polymers increased in direct proportion to the monomer conversion at all $SnBr_4$ concentrations. The apparent rate constant of polymerization (k_{app}) was obtained from the slope of the first-order plots. The plot of log(k_{app}) vs log([$SnBr_4$]) (Figure 7) gives a slope nearly equal to 1, suggesting a first-order dependence on $SnBr_4$ and the presence of $SnBr_4Cl^-$ counterions. For the cationic polymerization of St[22] in CH_2Cl_2, a first-order dependence of the polymerization rate on [$SnCl_4$] was already reported in the literature, and one can expect the first-order dependence on [$SnBr_4$] in the present polymerization system.

Control of Polymer Molecular Weight. So far, the living nature of the cationic polymerization of *p*-MeOSt was studied in the molecular range up to $M_n \approx 20\,000$. To confirm the absence of chain transfer and termination, a series of experiments were carried out by increasing the initial molar ratio of monomer to initiator ($[M]_0/[I]_0$), keeping all other conditions constant. The ($[M]_0/[I]_0$) ratio was varied from 180 to 900. As shown in Figure 8, the polymer molecular weights at 100% conversion are directly proportional to the ratio of *p*-MeOSt to *p*-MeOStCl. The M_n values are in acceptable agreement with those calculated with the assumption that each molecule of *p*-MeOStCl initiates one living

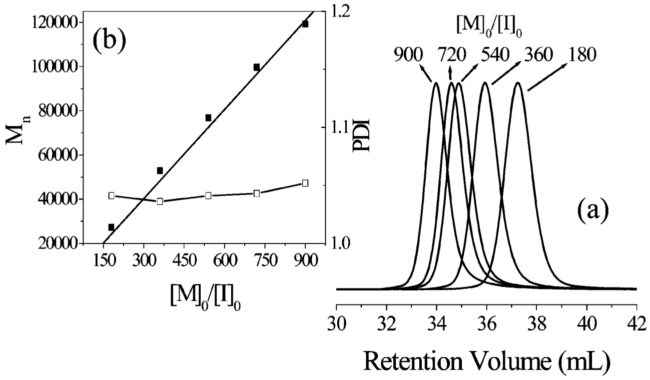


Figure 8. (a) GPC RI traces and (b) M_n and PDI vs $[M]_0/[I]_0$ of poly(*p*-MeOSt) in the polymerization of *p*-MeOSt initiated with *p*-MeOStCl/$SnBr_4$ at −30 °C in CH_2Cl_2; $[p\text{-MeOSt}]_0/[p\text{-MeOStCl}] = 180-900$ and $[SnBr_4] = 0.004$ mol L^{-1}, $[DTBP] = 0.006$ mol L^{-1}, $[p\text{-MeOStCl}] = 0.001$ mol L^{-1}, polymerization time was 24 min. In (b) ■: M_n; □: PDI; and straight line indicates the M_n based on 100% conversion.

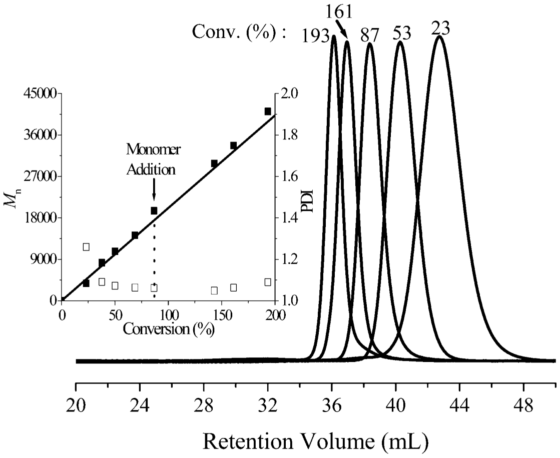


Figure 9. Monomer increment experiments in the cationic polymerization of *p*-MeOSt initiated with *p*-MeOStCl/$SnBr_4$ at −30 °C in CH_2Cl_2; $[p\text{-MeOSt}]_0 = [p\text{-MeOSt}]_{\text{increment}} = 0.15$ mol L^{-1}, $[p\text{-MeOStCl}] = 0.001$ mol L^{-1}, $[DTBP] = 0.006$ mol L^{-1}, and $[SnBr_4] = 0.004$ mol L^{-1}. (a) ■: M_n; □: PDI; and straight line indicates the M_n based on conversion. (b) GPC RI traces of poly(*p*-MeOSt) at different conversions.

polymer chain, and over the whole range of the $[M]_0/[I]_0$ ratio, the PDI of the polymers remained very narrow (PDI < 1.1). Thus, the present initiating system, *p*-MeOStCl/$SnBr_4$, efficiently generates high molecular weight poly(*p*-MeOSt) with very narrow PDI.

Chain Extension Experiment. The living nature of the *p*-MeOSt polymerization with the *p*-MeOStCl/$SnBr_4$ initiating system was further studied by chain extension; i.e., a new feed of *p*-MeOSt was added to the polymerization mixture before the initial charge of the monomer had been completely consumed. The additional *p*-MeOSt was smoothly polymerized at nearly the same rate as in the first stage. As shown in Figure 9, the M_n of poly(*p*-MeOSt) increased in direct proportion to monomer conversion and was very close to the theoretical value for living polymers. The molecular weight distribution remained very narrow (<1.1), and no tailing appeared in the low molecular weight region. Thus, the polymerization of *p*-MeOSt by *p*-MeOStCl/$SnBr_4$ initiating system in CH_2Cl_2 at −30 °C is living, as chain transfer and termination are undetectable.

Lifetime of the Living Ends. The lifetime of living poly(*p*-MeOSt) was studied by the incremental monomer addition technique. The unquenched polymerization reaction mixture was left at −30 °C under monomer-starved conditions for different times, and then after a certain time *p*-MeOSt in CH_2Cl_2 at −30 °C was added to polymerize for another 20 min. The GPC RI chromatograms (Figure 10) obtained after the polymerization of the second monomer increment become bimodal with increasing aging time. Thus, under monomer-starved conditions the polymeric chain ends are stable up to ~30 min in CH_2Cl_2 at −30 °C; however, they slowly decompose at longer time.

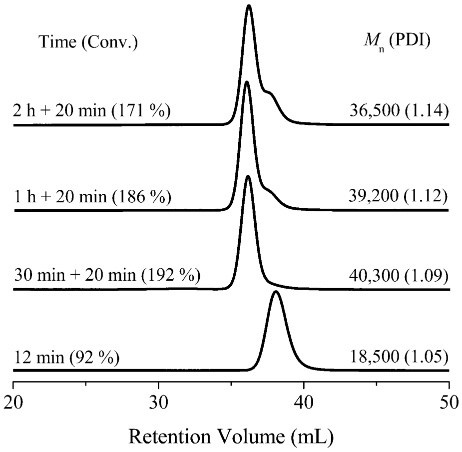


Figure 10. GPC RI traces of poly(*p*-MeOSt); $[p\text{-MeOSt}]_0 = [p\text{-MeOSt}]_{\text{increment}} = 0.15$ mol L^{-1}, $[p\text{-MeOStCl}] = 0.001$ mol L^{-1}, $[DTBP] = 0.006$ mol L^{-1}, and $[SnBr_4] = 0.004$ mol L^{-1} at −30 °C in CH_2Cl_2.

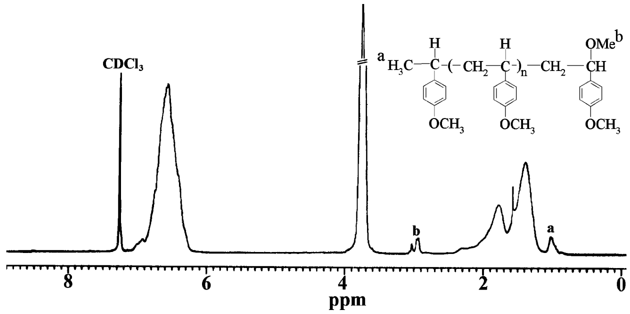


Figure 11. ^{1}H NMR spectrum of poly(*p*-MeOSt) obtained with *p*-MeOStCl/$SnBr_4$ initiating system in CH_2Cl_2 at −30 °C. $[p\text{-MeOSt}] = 0.15$ mol L^{-1}, $[p\text{-MeOStCl}] = 0.007$ mol L^{-1}, $[DTBP] = 0.006$ mol L^{-1}, and $[SnBr_4] = 0.004$ mol L^{-1} at 100% conversion; $M_{n,GPC} = 3300$ and PDI = 1.15.

In another experiment DTBP, $SnBr_4$, and *p*-MeOStCl were mixed in CH_2Cl_2 at −30 °C, and polymerization was started by the addition *p*-MeOSt after 0, 15, 30, 60, and 120 min and polymerized for 25 min. The M_ns of the polymers were 19 800, 21 500, 24 400, 26 700, and 28 400 respectively when *p*-MeOSt was added after 0, 15, 30, 60, and 120 min to the premixed DTBP, $SnBr_4$, and *p*-MeOStCl in CH_2Cl_2 at −30 °C. The PDI, however, remained unchanged (1.05−1.07). This indicates that monomeric chain end also decomposes (most likely eliminates H^+ which is trapped by DTBP) with increasing aging time in the presence of $SnBr_4$, and the initiator efficiency decreases from ~100% to ~71% in 120 min.

Analysis of the End Group. The ^{1}H NMR spectroscopy was used to study the end group structure of the polymers. Figure 11 depicts the ^{1}H NMR spectrum of a typical poly(*p*-MeOSt) sample obtained with the *p*-MeOStCl/$SnBr_4$ initiating system in CH_2Cl_2 at −30 °C at 100% conversion; $M_{n,GPC} = 3300$ and PDI = 1.15. The

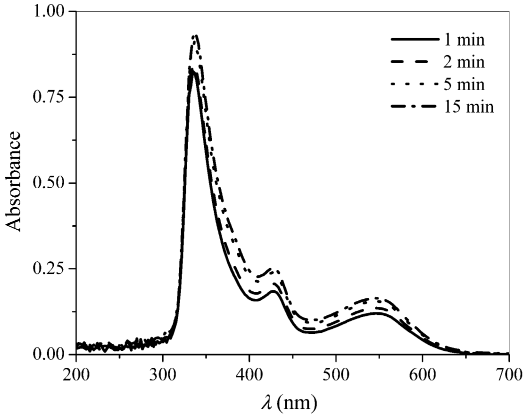


Figure 12. Plots of absorption at different time for the ionization of *p*-MeOStCl with $SnBr_4$; [*p*-MeOStCl] = 0.03 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, and [$SnBr_4$] = 0.08 mol L^{-1} in CH_2Cl_2 solvent at −60 °C.

signals at 6.25−7.05 and 3.6−4.0 ppm are due to the aromatic protons and $-OCH_3$ protons attached to the aromatic ring, respectively. The signals at 1.2−2.4 ppm are due to the $-CH_2$ and −CH protons in the main chain of the polymer. The peak at 0.93−1.1 ppm corresponds to the H_3C- protons from the initiator fragment (*p*-MeOStCl). The peak at 2.92−3.08 ppm is due to methoxy terminal group resulting from a reaction with methanol. MALDI−TOF MS measurements also confirmed the methoxy end group,; the peaks were consistent with $CH_3-CH(C_6H_4-OCH_3)-(-CH_2-CH(C_6H_4-OCH_3))_n-OCH_3$. The methoxy end group, however, is not the result of in situ termination of cations since the cation concentration is very low (see later). More likely fast methanolysis of the chloro end yields the methoxy end groups. The number-average degree of polymerization for poly(*p*-MeOSt) determined from the ^1H NMR spectrum as $M_{n,NMR}$ = 3500 (from the peak intensity ratio of the $-OCH_3$ protons attached to the aromatic ring at 3.6−4.0 ppm to the H_3C- terminal group at 0.93−1.1 ppm) is in reasonable agreement with the calculated value based on the assumption that one living chain is formed from one molecule of initiator, *p*-MeOStCl. On the basis of the above discussion and in agreement with the molecular weight analysis, the general formula of poly(*p*-MeOSt) can be written as shown in Figure 11.

Determination of the Absolute Rate Constant of Propagation ($k_p^{\pm}$) of the Cationic Polymerization of *p*-MeOSt. a. UV−Vis Spectroscopy. To determine the equilibrium constant of ionization (K_i), the ionization of the model compound *p*-MeOStCl with $SnBr_4$ was studied by UV−vis spectroscopy in CH_2Cl_2 at −30 and −60 °C. Mixing *p*-MeOStCl with the solution of DTBP and $SnBr_4$ in CH_2Cl_2 at −60 °C under stirring, the UV−vis spectrum exhibited a maximum absorption at 344−348 nm. Also, as shown in Figure 12, two other peaks centered at 427 and 550 nm developed. The intensity of these peaks is much higher at the higher temperature (−30 °C) under the same conditions. As we discussed earlier, the peak at 344−348 nm is due to the *p*-MeOSt cation and was used to determine the K_i. The plot of absorbance vs $SnBr_4$ concentration showed a positive intercept for both temperatures. This intercept is due to the impurities (possibly *p*-methoxyacetophenone) present in the commercially available *p*-MeOSt. A similar observation was also observed during the ionization of hydrochlorinated 2,4,6-trimethylstyrene. This value of the intercept was subtracted from the original absorbance, and percent ionization was calculated using the corrected value of absorbance. The molar absorption coefficient ϵ_{max} = 27 300 L mol^{-1} cm^{-1} was determined from the absorption spectrum of *p*-MeOStCl at 345 nm with $TiCl_4$ at −30 °C. A further increment of $TiCl_4$ confirmed the quantitative ionization of *p*-MeOStCl to the *p*-MeOSt$^+$ cation. This ϵ_{max} value is in excellent agreement with the value reported in the literature for *p*-MeOSt cation[14c,23] (ϵ_{max} = 28 000 L mol^{-1} cm^{-1} at room temperature) and *p*-methoxy-α-methylstyrene cation[24] (ϵ_{max} = 28 500 L mol^{-1} cm^{-1} at −72 °C). From the results presented in Figure 13 the average equilibrium constant of ionization, $K_i = 9.16 \times 10^{-3}$ L mol^{-1} and $K_i = 3.11 \times 10^{-2}$ L mol^{-1}, was calculated for −30 and −60 °C, respectively.

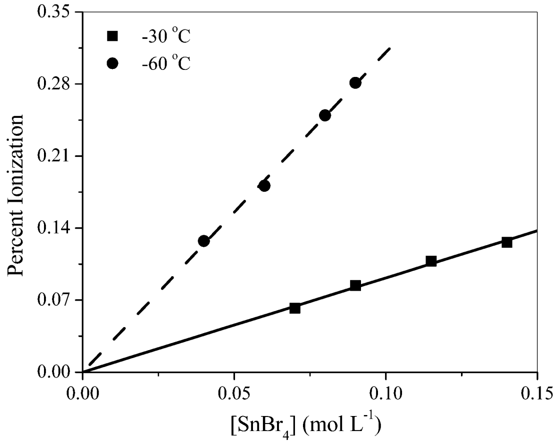


Figure 13. Ionization of *p*-MeOStCl by $SnBr_4$ in CH_2Cl_2 at −30 and −60 °C; [*p*-MeOStCl]$_0$ = 0.04 mol L^{-1} (−30 °C), 0.03 mol L^{-1} (−60 °C) and [DTBP] = 0.006 mol L^{-1}.

During the polymerization of *p*-MeOSt, ion pairs are considered as active species since in the presence of DTBP, ion-pair dissociation is suppressed[1,25] by common anions of the pyridinium salt formed from existing traces of moisture in the presence of $SnBr_4$. The rate of polymerization (R_p) can be expressed as

$$R_p = -d[p\text{-MeOSt}]/dt = k_p^{\pm}[P_n^+][p\text{-MeOSt}] = k_{app}[p\text{-MeOSt}] \quad (1)$$

where [P_n^+] is the concentration of the active center, [*p*-MeOSt] is the concentration of the monomer (M), and k_{app} is the first-order apparent rate constant of propagation obtained from the first-order plot of ln([M]$_0$/[M]) vs time. After integration, eq 1 can be expressed as

$$\ln\frac{[M]_0}{[M]_t} = k_{app}t = k_p^{\pm}K_i[SnBr_4][P_n-Cl]_0 t \qquad (2)$$

where K_i is the equilibrium constant of ionization and [P_n−Cl] is the concentration of total chain ends. At −30 °C, the plot of ln([M]$_0$/[M]) vs time (Figure 2) gives the slope = $k_{app} = 3.9 \times 10^{-3}$ s^{-1}. Using $K_i = 9.16 \times 10^{-3}$ L mol^{-1}, [$SnBr_4$] = 0.004 mol L^{-1}, and [*p*-MeOStCl] = 0.001 mol L^{-1}, [P_n^+] = 3.664×10^{-8} mol L^{-1} was calculated at −30 °C. Using k_{app}, $k_p^{\pm} = 1.07 \times 10^5$ L mol^{-1} s^{-1} was obtained at −30 °C. By a similar calculation, $k_p^{\pm} = 3.83 \times 10^4$ L mol^{-1} s^{-1} was obtained for −60 °C.

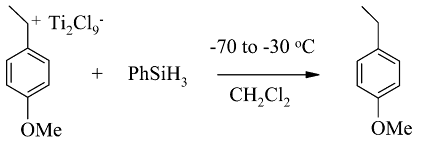
b. Competition Experiments. Recently competition experiments have been successfully used to determine

Table 2. Competition Experiment of *p*-MeOSt with Phenylsilane Capping Agent in CH_2Cl_2 Using $SnBr_4$[a]

temp (°C)	$k_c^{\pm}$ (L mol^{-1} s^{-1})	conv (%)	M_n (GPC)	PDI	$k_p^{\pm}/k_c^{\pm}$ (X_{∞}^{M})	$k_p^{\pm}/k_c^{\pm}$ ($DP_{n,\infty}$)	$k_p^{\pm} \times 10^{-4}$ (L mol^{-1} s^{-1})
−30	340.1	59.2	12 300	1.2	538	566	18.8
−40	188.6	50.3	10 700	1.3	419	455	8.2
−50	99.4	65.9	13 400	1.2	645	657	6.5
−60	49.4	62.6	12 900	1.2	590	614	3.0

[a] [*p*-MeOStCl] = 0.001 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [*p*-MeOSt] = 0.15 mol L^{-1}, [$SnBr_4$] = 0.004 mol L^{-1}, and [phenylsilane] = 0.6 mol L^{-1}.

Scheme 1



$\Delta H^{\#} = 25.791 \pm 1.284$ kJ mol^{-1}

$\Delta S^{\#} = -88.614 \pm 5.908$ J mol^{-1} K^{-1}

$k_p^{\pm}$ for the cationic polymerization of IB,[1] St,[2] and TMeSt.[5] In the competition experiments the polymerizations are carried out in the presence of a suitable trapping/terminating agent at well-chosen concentrations, so conversion (X_{∞}^{M}) and the number-average degree of polymerization ($DP_{n,\infty}$) reach limiting values. The reactivity ratio ($k_p^{\pm}/k_c^{\pm}$) can be calculated from both X_{∞}^{M} and $DP_{n,\infty}$ using eqs 3 and 4.

$$\frac{k_p^{\ \pm}}{k_c^{\ \pm}} = \frac{\ln(1 - X_{\infty}^{\ M})}{\ln(1 - [p\text{-MeOStCl}]_0/[\text{PhSi}]_0)} \qquad (3)$$

$$\frac{k_p^{\ \pm}}{k_c^{\ \pm}} = \frac{\ln(1 - \text{DP}_{n,\infty}[p\text{-MeOStCl}]_0/[p\text{-MeOSt}]_0)}{\ln(1 - [p\text{-MeOStCl}]_0/[\text{PhSi}]_0)} \qquad (4)$$

In eqs 3 and 4, $[p\text{-MeOStCl}]_0$ is the initial concentration of the initiator, which equals that of the chain ends, $[\text{PhSi}]_0$ is the initial concentration of the capping agent, phenylsilane, and $[p\text{-MeOSt}]_0$ is the initial concentration of the monomer. Using eqs 3 and 4, $k_p^{\pm}$ can be calculated if $k_c^{\pm}$ is known. The $k_c^{\pm}$ values at different temperatures have been determined for the reaction of *p*-$MeOSt^+$ cation with phenylsilane in CH_2Cl_2,[26] and the Eyring parameters are reported in Scheme 1. The $k_c^{\pm}$ values used for the calculation of $k_p^{\pm}$ at different temperatures are presented in Table 2.

Since the $k_c^{\pm}$ is known for the reaction of phenylsilane to the *p*-MeOSt cation in CH_2Cl_2 at different temperatures, the polymerization of *p*-MeOSt was carried out in the presence of phenylsilane with the *p*-MeOStCl/$SnBr_4$ initiating system in CH_2Cl_2 in the presence of DTBP as proton trap. First, the time necessary to reach limiting conversion was determined at −30 °C. Limiting conversion was reached in less than 60 min, suggesting complete capping of the polymer cation. Therefore, competition experiments at other temperatures were also carried out for 60 min. The limiting conversions, limiting M_n's, and the calculated $k_p^{\pm}$ values at all temperature are shown in Table 2. Table 2 also shows that the molecular weight distribution of the polymers obtained in the competition experiments is much narrower (PDI ~ 1.2−1.3) than the expected most probable distribution (PDI ~ 2) for bimolecular termination. While at −30 °C the limiting conversion was 59.2% when $SnBr_4$ was added to the mixture of initiator, *p*MeOSt, and phenylsilane, the limiting conversion was only ~20% when $SnBr_4$ and phenylsilane were premixed and added last to initiate the polymerization under the same conditions. Using $SnCl_4$ or the mixture of ($SnCl_4$ + phenylsilane) in the competition experiment at −30 °C, 64.6% and 36.8% limiting conversions were obtained, respectively. This suggests a complex nature of the reaction, which may be due to hydride transfer from phenylsilane to Sn halides. Hydride transfer from ordinary silanes to weak Lewis acids such as BCl_3 has already been reported.[27] It is also known that $TiCl_4$ does not react with ordinary silanes at low temperature.[28] Therefore, $TiCl_4$ was used in further competition experiments, and indeed at −30 °C the limiting conversions were almost the same when the polymerization experiments were carried out by adding $TiCl_4$ or the mixture of $TiCl_4$ and phenylsilane.

Table 3. Competition Experiment of *p*-MeOSt with Phenylsilane Capping Agent in CH_2Cl_2 Using $TiCl_4$[a]

temp (°C)	$k_c^{\pm}$ (L mol^{-1} s^{-1})	conv (%)	M_n (GPC)	PDI	$k_p^{\pm} \times 10^{-4}$ (L mol^{-1} s^{-1})
−30	340.1	35.3	7400	2.7	11.4
−40	188.6	34.3	7600	2.9	6.3
−50	99.4	39.7	8700	2.7	4.0
−60	49.4	39.9	8300	2.8	1.9

[a] [*p*-MeOStCl] = 0.001 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [*p*-MeOSt] = 0.15 mol L^{-1}, [$TiCl_4$] = 0.003 mol L^{-1}, and [phenylsilane] = 0.75 mol L^{-1}.

Using [$TiCl_4$] = 0.003 mol L^{-1}, competition experiments were carried out at different temperatures. Limiting conversions indicated in Table 3 were reached in less than 5 min. The calculated $k_p^{\pm}$ values are also listed in Table 3. The ^1H NMR spectrum confirms the absence of methoxy chain ends in the polymers obtained in the competition experiments. Also, the MALDI−TOF MS analysis revealed that the end group is −H for the poly(*p*-MeOSt) obtained from the competition experiment of *p*-MeOSt with phenylsilane capping agent in CH_2Cl_2 using $TiCl_4$. The peaks were consistent with the chemical structure $CH_3-CH(C_6H_4-OCH_3)-(-CH_2-CH(C_6H_4-OCH_3))_n-H$.

The reactivity ratios were calculated from X_{∞}^{M} using eq 3 and from the $DP_{n,\infty}$ using eq 4. These two methods yielded similar $k_p^{\pm}/k_c^{\pm}$ values. Using the $k_c^{\pm}$ value at a certain temperature, $k_p^{\pm}$ at the corresponding temperature was calculated from the average of $k_p^{\pm}/k_c^{\pm}$ values obtained from eqs 3 and 4, respectively. Table 3 shows that $k_p^{\pm}$ is greatly dependent on temperature and increases considerably with increasing temperature. Figure 14 exhibits the Arrhenius plot of the data as ln($k_p^{\pm}$) vs $1/T$; from the slope, the activation energy of propagation, E_a^{p}, was calculated to be 24.9 kJ mol^{-1}.

According to Table 3 $k_p^{\pm} = 1.1 \times 10^5$ L mol^{-1} s^{-1} at −30 °C and decreases to 1.9×10^4 L mol^{-1} s^{-1} at −60 °C. These values are similar to that obtained with $SnBr_4$ listed in Table 2; however, because of the unexpectedly low polydispersities we cannot consider these values. The different nature of the Lewis acids employed in the

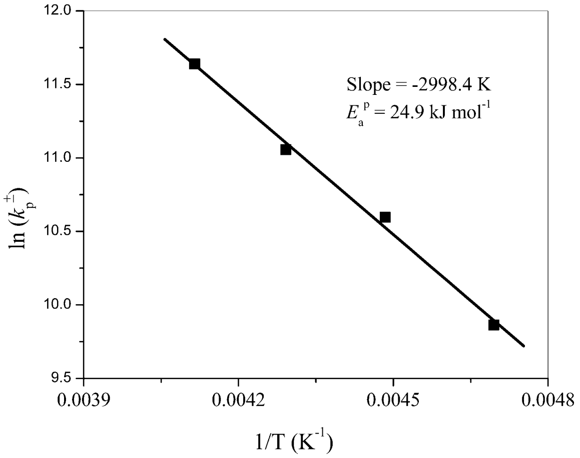


Figure 14. Arrhenius plot of $\ln(k_p^{\pm})$ vs $1/T$ to determine activation energy of propagation, E_a^p.

classical method and competition does not prevent a direct comparison the $k_p^{\pm}$ values obtained, since the propagation rate constant is independent of the nature of Lewis acid.[1,2] In this comparison we find that the two methods yield similar propagation rate constants.

Conclusion

The living carbocationic polymerization of *p*-MeOSt can be achieved using the 1-chloro-1-(*p*-methoxyphenyl)-ethane (*p*-MeOStCl)/$SnBr_4$ initiating system in CH_2Cl_2 at −60 to −20 °C. Polymerization rates, M_ns, and PDIs are unaffected by excess DTBP. The polymerization is first order in [$SnBr_4$], which suggests the presence of $SnBr_4Cl^-$ counterions. The propagating chain end of poly(*p*-MeOSt) has very similar stability to that of monomeric chain end of *p*-$MeOSt^+$ cation.

Both UV−vis spectroscopy and competition experiments can be used to determine the absolute rate constant of propagation for ion pairs for the living cationic polymerization of *p*-MeOSt. The $k_p^{\pm}$ value increases (activation energy of propagation = 24.9 kJ mol^{-1}) and the overall polymerization rate decreases with increasing temperature (apparent activation energy of propagation = −3.5 kJ mol^{-1}). This is attributed to a larger decrease in the active center concentration with increasing temperature compared to the corresponding increase in $k_p^{\pm}$. The $k_p^{\pm}$ values obtained from the two methods are similar, confirming the general applicability of the competition experiments for the determination of absolute rate constants of propagation in carbocationic polymerization.

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Supporting Information Available: MALDI-TOF-MS spectra of poly(*p*-MeOSt) and plots of absorption−time for ionization of *p*-MeOStCl with $SnBr_4$ and $TiCl_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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