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Determination of the Propagation Rate Constant in the Carbocationic Polymerization of 2,4,6-Trimethylstyrene

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ABSTRACT: The living carbocationic polymerization of 2,4,6-trimethylstyrene (TMeSt) was studied using the 1-chloro-1-(2,4,6-trimethylphenyl)ethane/BCl_3 initiating system in CH_2Cl_2 from −70 to −20 °C. The equilibrium constant of ionization (K_i) was calculated from the cation concentration determined by UV−visible spectroscopy. From the apparent rate constant of propagation (k_p^{app}) and K_i, the absolute rate constant of propagation for ion pairs $k_p^{\pm} = 1.4 \times 10^4$ L mol^{-1} s^{-1} was calculated at −70 °C. The rate constant of ion collapse, k_{-i} was determined from the polydispersity vs conversion plots. From K_i and k_{-i}, the rate constant of ionization, k_i were also calculated. From the temperature dependence of K_i, and k_{-i} the enthalpy and entropy of the ionization and deactivation were obtained, respectively. Competition experiments i.e., polymerization carried out in the presence of 2-chloropropene as a π-nucleophile, were also carried out at −70 °C to determine $k_p^{\pm}$ separately. NMR spectroscopy, gel permeation chromatography, and elemental analysis suggested complete capping of the polymeric cation and the absence of side reactions. From the limiting number-average degree of polymerization and the known rate constant of capping $k_c = 62.0$ L mol^{-1} s^{-1}, $k_p^{\pm} = 8.3 \times 10^4$ L mol^{-1} s^{-1} was determined. This value is similar to that determined from k_p^{app} and K_i; thus, the utility of competition experiments is corroborated.

Introduction

We recently reported the absolute rate constants of propagation for ion pairs ($k_p^{\pm}$) determined by two different diffusion clock methods in the cationic homopolymerization of isobutylene (IB)[1,2] and styrene (St).[3] The $k_p^{\pm}$ values agreed well with those predicted by the linear free energy relationship (LFER) by Mayr;[4] however, they were 4−6 orders of magnitude higher than previously accepted values.[5] This discrepancy was ascribed to largely overestimated values of active center concentration by previous authors. In the case of St and derivatives UV spectroscopy could be used to determine the concentration of active centers and hence the propagation rate constants; however, identification of the fraction of the absorption that is due to propagating species is necessary when various side reactions, e.g., isomerization, inter- and intramolecular alkylation, etc. may take place. In the cationic polymerization of St, one of the major side reactions is indanic cyclization.[6] Intra- and intermolecular alkylation are absent in the cationic polymerization of 2,4,6-trimethylstyrene (TMeSt), which was recognized in an early report on the living polymerization of TMeSt initiated by the cumyl acetate/BCl_3 initiating system in CH_3Cl at −30 °C.[7] We have recently reexamined the polymerization of TMeSt initiated by the 2,4,6-trimethylstyryl cation, a model propagating end in CH_2Cl_2 at −70 °C, and observed living polymerization yielding polymers with theoretical molecular weights and very low polydispersity indices (M_w/M_n = 1.02 to 1.1).[8] Since side reactions of the TMeSt cation are absent, the equilibrium constant of ionization (K_i) could be determined by UV spectroscopy and from the active chain end concentration and the rate of polymerization, $k_p^{\pm}$ may be calculated. Therefore, TMeSt is a highly suitable monomer to compare $k_p^{\pm}$ values predicted by LFER to that obtained by direct measurement and to the propagation rate constant obtained in competition experiments (used previously with IB and St). In the present study, we report on results of these kinetic studies in the living cationic polymerization of 2,4,6-trimethylstyrene.

Experimental Section

Materials. TMeSt (Aldrich, 95%) was freed from inhibitor by washing with 5% NaOH and then repeatedly with water. After drying over anhydrous Na_2SO_4, it was distilled from calcium hydride under reduced pressure. The initiator 1-chloro-1-(2,4,6-trimethylphenyl)ethane (TMeStCl) was synthesized by hydrochlorination of TMeSt in CH_2Cl_2 (TMeSt/CH_2Cl_2, 1/10 (v/v)) at 0 °C and after removing CH_2Cl_2 in the rotary evaporator it was purified by vacuum distillation from calcium hydride. ^{1}H NMR: 6.92 (s), 5.67 (q), 2.56 (s), 2.29 (s), and 1.95 ppm (d). BCl_3 (99.9%, Aldrich) and di-*tert*-butylpyridine (DTBP, 97+ %, Aldrich) were used as received. Commercial 2-chloropropene (98%, Aldrich) (may contain HCl as impurity, which can initiate polymerization during the competition experiment) was distilled from NaOH at 20 °C just before use and collected in a round-bottom flask cooled by dry ice. The CH_2Cl_2 was shaken three times with 5% NaOH and then repeatedly with water. It was predried with anhydrous Na_2SO_4, and distilled from calcium hydride under nitrogen. This distilled CH_2Cl_2 was refluxed under nitrogen overnight with phosphorus pentoxide and distilled to a round-bottom flask over phosphorus pentoxide. It was refluxed under nitrogen overnight and distilled just before use. Other chemicals and solvents were purified as described previously or used as received.[1,2]

Polymerization. Polymerizations were carried out under a dry nitrogen atmosphere ([H_2O] < 1.0 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 20 mL. At predetermined time intervals, the polymerizations were

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quenched with excess prechilled methanol. The polymer was recovered and purified by reprecipitation from CH_2Cl_2/methanol. Monomer conversions were determined by gravimetric analysis. As a typical example; the polymerization was carried out in CH_2Cl_2 at −70 °C using the following condition: [TMeStCl] = 0.001 mol L^{-1}, [DTBP] = 0.003 mol L^{-1}, [TMeSt] = 0.136 mol L^{-1}, [BCl_3] = 0.053 mol L^{-1}. Into a 75 mL culture tube at −70 °C were added 19.6 mL of CH_2Cl_2 at room temperature, 0.6 mL of DTBP stock solution in CH_2Cl_2 (0.1 mol L^{-1}) at −70 °C, 0.5 mL of TMeStCl stock solution in CH_2Cl_2 (0.04 mol L^{-1}) at −70 °C, and 0.44 mL of TMeSt at room temperature and mixed thoroughly. The polymerization was started by the addition of 1.06 mL of BCl_3 solution (1.0 mol L^{-1}, in CH_2Cl_2) at −70 °C. After a predetermined time (16 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 316 mg of polymer (conversion = 79.5%, $M_{n,GPC}$ = 15550, PDI = 1.04).

Competition experiments were carried out in the presence of 2-chloropropene as a nucleophile. In a typical competition experiment the polymerization was carried out in CH_2Cl_2 at −70 °C using the following concentration: [TMeStCl] = 0.001 mol L^{-1}, [DTBP] = 0.003 mol L^{-1}, [TMeSt] = 0.05 mol L^{-1}, [BCl_3] = 0.053 mol L^{-1}, [2-chloropropene] = 3 mol L^{-1}. Into a 75 mL culture tube at −70 °C were added 14.1 mL of CH_2Cl_2 at room temperature, 0.6 mL of DTBP stock solution in CH_2Cl_2 (0.1 mol L^{-1}) at −70 °C, 0.5 mL of TMeStCl stock solution in CH_2Cl_2 (0.04 mol L^{-1}) at −70 °C, 0.16 mL of TMeSt at room temperature and 5.1 mL of 2-chloropropene at −70 °C and mixed thoroughly. The polymerization was started by the addition of 1.06 mL of BCl_3 solution (1.0 mol L^{-1}, in CH_2Cl_2) at −70 °C. After a predetermined time (30 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 71 mg of polymer (conversion = 48.6%, $M_{n,GPC}$ = 2600, PDI = 1.7).

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. THF was used as eluent at a flow rate of 1.0 mL/min at room temperature. The molecular weights and polydispersities were determined using the universal calibration curve and Viscotek TriSEC GPC software. The differential refractive index increment (dn/dc) measurement at 25 °C was performed on an OPTILAB DSP Interferometric refractometer, using a P10 flow cell (1 mm path length). The dn/dc for poly(2,4,6-trimethylstyrene) was found to be 0.203 mL/g. The ^1H NMR spectroscopy was carried out on a Bruker 250 MHz spectrometer using $CDCl_3$ as a solvent (Cambridge Isotope Lab., Inc.). The ^{13}C NMR spectrum was recorded on a Bruker 500 MHz spectrometer using $CDCl_3$ as a solvent. The elemental analysis was done by Galbraith Laboratories, Inc. (Knoxville, TN).

UV—Visible Spectroscopy. For the UV−visible spectroscopic measurements a quartz immersion probe 661.300-QX (Hellma, optical path: 0.5 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 "Aspect Plus" software (Zeiss). UV−visible reactions were carried out at −70 °C in CH_2Cl_2 under a dry nitrogen atmosphere in the glovebox using [TMeStCl] = 0.1 mol L^{-1} and [DTBP] = 0.003 mol L^{-1} and with different BCl_3 concentrations.

Results and Discussion

Living Polymerization of TMeSt Initiated by TMeStCl/BCl_3 in CH_2Cl_2. The cationic polymerization of TMeSt was carried out using TMeStCl as initiator in conjunction with BCl_3 in the presence of DTBP as proton trap in CH_2Cl_2 in the temperature range of −20 to −70 °C. The first-order plots of ln([M]$_0$/[M]) vs time were linear at all temperatures, indicating the absence of irreversible termination during the polymerization. Representative plots for −20, −40 and −70 °C are shown in Figure 1. The slope of the first-order plot represents the apparent rate constant for propagation (k_p^{app}). The number-average molecular weight (M_n) vs conversion plots for −20, −40 and −70 °C are shown in Figure 2. The molecular weights 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 polydispersity index (M_w/M_n) decreases with increasing conversion due to the dynamic exchange between dormant and living centers. The linear M_n−conversion plot together with the linear first-order plots, indicate that the polymerization is living at all temperatures studied here. The experimental M_ns are close to the theoretical M_ns based on conversion, demonstrating close to 100% initiator efficiency.

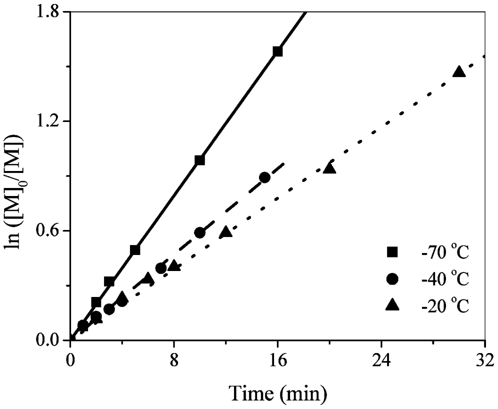

Figure 1. First-order plot of ln([M]$_0$/[M]) vs time for the cationic polymerization of TMeSt initiated by TMeStCl/BCl_3 in CH_2Cl_2 at different temperatures. [TMeStCl] = 0.001 mol L^{-1}, [DTBP] = 0.003 mol L^{-1}, [TMeSt] = 0.136 mol L^{-1}, and [BCl_3] = 0.053 mol L^{-1}

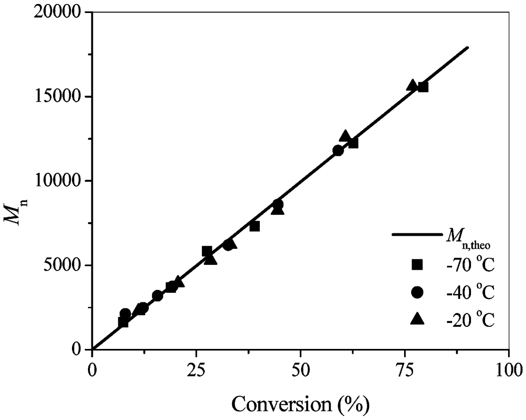

Figure 2. Variation of M_n with conversion at different temperatures. Reaction conditions are the same as in Figure 1. The straight line indicates the M_n, assuming that one polymer chain forms per molecule of TMeStCl.

Control experiments were also carried out in the absence of initiator, TMeStCl (direct initiation). Under the same conditions, 10.0%, 16.2%, 25.8%, 48.8%, and 61.8% monomer conversions were obtained at −70 °C after 15 and 30 min and 1, 2, and 3 h, respectively. This confirms that direct initiation is operational but is much slower than in the presence of initiator, TMeStCl, and the kinetics of the polymerization is unaffected.

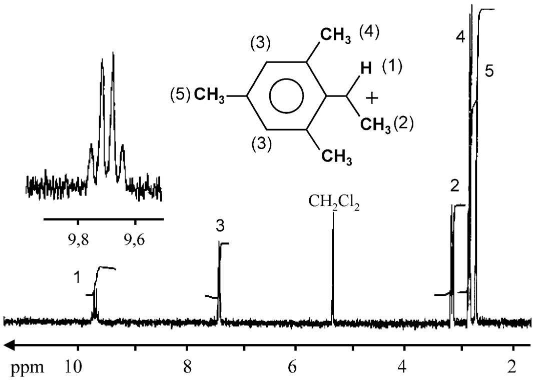

Figure 3. ^{1}H NMR spectrum of $TMeSt^+$ obtained from TMeStCl (0.072 mol L^{-1}) and $GaCl_3$ (0.145 mol L^{-1}) in CD_2Cl_2 at −78 °C.

Determination of the Equilibrium Constant of Ionization, K_i. Low temperature ^{1}H NMR spectroscopy was used to study the stability and ionization of TMeStCl. The ^{1}H NMR spectrum of $TMeSt^+$ cation was studied from −78 °C to −30 °C. The ^{1}H spectrum of $TMeSt^+$ obtained from TMeStCl (0.072 mol L^{-1}) and $GaCl_3$ (0.145 mol L^{-1}) in CD_2Cl_2 at −78 °C is shown in Figure 3. Two equivalents of $GaCl_3$ are required for complete ionization, which may suggest the presence of dimeric $Ga_2Cl_7^-$ counteranions. Complete ionization was confirmed by the absence of characteristic resonance peaks for TMeStCl and the spectrum at −78 to −30 °C shows exclusively the resonances of the cation. On the basis of ^{1}H NMR spectroscopy the trimethylstyryl cation ($TMeSt^+$) appears perfectly stable in the temperature range −78 to −30 °C.

In line with the high stability of the TMeSt cation directly observed with $GaCl_3$ as Lewis acid, side reactions were absent with BCl_3 and living polymerization of TMeSt in conjunction with this Lewis acid was observed in the studied −20 to −70 °C temperature range. Therefore, in separate experiments we attempted spectroscopic determination of the equilibrium constant of ionization, K_i. In the previous paper in this issue it was shown that the reactivity of the monomeric and dimeric cations of TMeSt do not differ,[9] thus, the model compound TMeStCl was employed to determine K_i. Preliminary experiments, however, demonstrated that commercially available TMeSt, a precursor of TMeStCl, contains residual traces of 2,4,6-trimethylacetophenone, whose complex with BCl_3 gives UV absorption at a similar wavelength (λ_{max} = 325 nm) to the trimethylstyryl cation. As a consequence the absorbance vs [BCl_3] plot was linear but exhibited a positive intercept. Distillation did not remove this impurity; therefore TMeSt was passed through a silica gel column using hexane as eluent before hydrochlorination to synthesize TMeStCl. This fast chromatographic method eliminated 2,4,6-trimethylacetophenone completely as confirmed by GC − MS.

The ionization of TMeStCl with BCl_3 was studied in CH_2Cl_2 at −70 °C using [TMeStCl] = 0.1 mol L^{-1} and [DTBP] = 0.003 mol L^{-1}. Ionization of TMeStCl was monitored by the strong UV absorption at 334 nm (ϵ = 25 000 L mol^{-1} cm^{-1}). Similar λ_{max} and ϵ were previously found[10] (λ_{max} = 335 nm, ϵ = 25 700 L mol^{-1} cm^{-1}) using $GaCl_3$. The absorbance at 334 nm and accordingly the percent ionization changed linearly with the BCl_3 concentration in 0.02−0.1 mol L^{-1} range (Figure 4). The plot in Figure 4 starts from the origin confirming the absence of the ketone impurity. From the results presented in Figure 4 the average equilibrium constant of ionization $K_i = 2.3 \times 10^{-3}$ L mol^{-1} was calculated at −70 °C using the equation; $K_i = [TMeSt^+BCl_4^-]/([TMeStCl][BCl_3])$, where $TMeSt^+BCl_4^-$ is the concentration of ion pairs. The K_i values were also determined at different temperatures (Figure 5), which allowed us to calculate the enthalpy of ionization (ΔH_i = −14.8 kJ mol^{-1}).

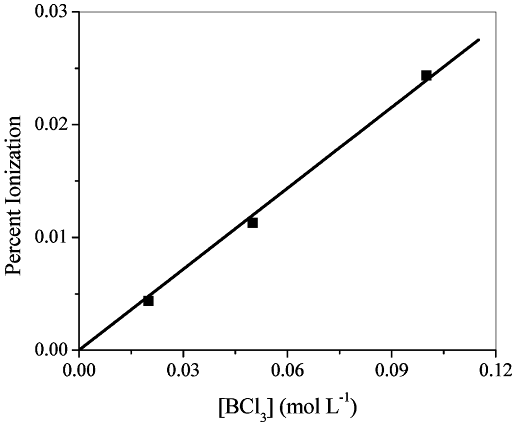

Figure 4. Ionization of TMeStCl by BCl_3 in CH_2Cl_2 at −70 °C; [TMeStCl] = 0.1 mol L^{-1} and [DTBP] = 0.003 mol L^{-1}.

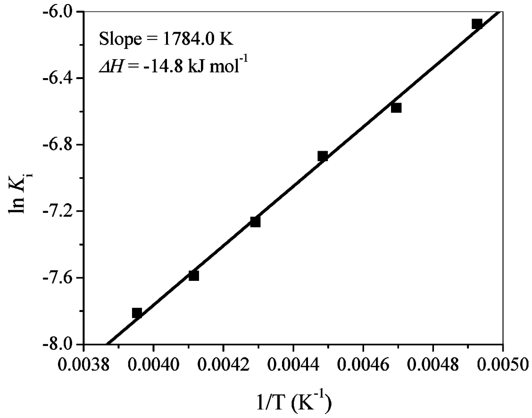

Figure 5. Van't Hoff plot of the equilibrium constant of ionization to calculate the enthalpy of ionization.

Kinetics of the Polymerization of TMeSt Initiated by TMeStCl/BCl_3 in CH_2Cl_2. In this article, all kinetic data are treated in terms of living cationic polymerization, where equilibrium exists between dormant (P_nCl) and propagating chain ends ($P_n^+BCl_4^-$) as shown in eq 1.

$$P_nCl + BCl_3 \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} P_n^+BCl_4^- \tag{1}$$

Here, k_i is the rate constant of ionization and k_{-i} is the rate constant of ion collapse (deactivation). Only ion pairs are considered as active species since in the presence of proton trap DTBP, ion pair dissociation is suppressed by common anions of the pyridinium salt formed from existing traces of moisture in the presence of BCl_3. The rate of polymerization (R_p) can be expressed as

$$R_p = -d[TMeSt]/dt = k_p^{\pm}[P_n^+BCl_4^-][TMeSt] = k_p^{app}[TMeSt] \tag{2}$$

Table 1. Kinetic Parameters for the Living Cationic Polymerization of TMeSt[a]

T (°C)	β	k_p^{app} (s^{-1})	K_i ($L\ mol^{-1}$)	k_{-i} (s^{-1})	$k_p^{\pm}$ ($L\ mol^{-1}\ s^{-1}$)	k_i ($L\ mol^{-1}\ s^{-1}$)
−70	104.9	1.65×10^{-3}	2.30×10^{-3}	1420.3	1.35×10^{4}	3.27
−60	119.0	1.34×10^{-3}	1.39×10^{-3}	2164.0	1.82×10^{4}	3.01
−50	133.6	1.17×10^{-3}	1.04×10^{-3}	2835.0	2.12×10^{4}	2.95
−40	146.6	9.81×10^{-4}	7.00×10^{-4}	3876.7	2.64×10^{4}	2.71
−30	164.9	9.42×10^{-4}	5.07×10^{-4}	5779.1	3.51×10^{4}	2.93
−20	184.5	8.11×10^{-4}	4.05×10^{-4}	6971.6	3.78×10^{4}	2.82

[a] [DTBP] = 0.003 mol L^{-1}, [TMeSt] = 0.136 mol L^{-1}, [TMeStCl] = 0.001 mol L^{-1}, and [BCl_3] = 0.053 mol L^{-1} in CH_2Cl_2.

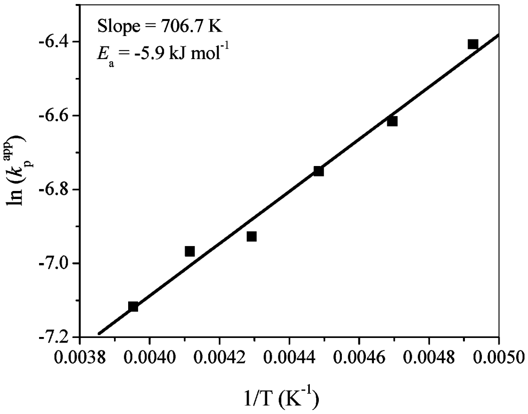

Figure 6. Arrhenius plot of the apparent rate constant of propagation to determine the apparent energy of activation, E_a.

where [$P_n^+BCl_4^-$] is the ion pair concentration, [TMeSt] is the concentration of the monomer (M) and k_p^{app} is the first-order apparent rate constant of propagation obtained from the first-order plot of ln($[M]_0/[M]$) vs time. The values of k_p^{app} at different temperatures are reported in Table 1. After integration, eq 2 yields eq 3

$$\ln\frac{[\mathrm{TMeSt}]_0}{[\mathrm{TMeSt}]_t} = k_p^{\ app}t = k_p^{\ \pm}K_i[\mathrm{BCl_3}][\mathrm{P}_n\mathrm{Cl}]_0 t \qquad (3)$$

where K_i is the equilibrium constant of ionization and [P_nCl] is the concentration of the dormant end, which since the extent of ionization is small, closely equals the total chain end concentration. At −70 °C, the plot of ln($[M]_0/[M]$) vs time (Figure 1) gives the slope, $k_p^{app} = 1.65 \times 10^{-3}\ s^{-1}$. Using $K_i = 2.3 \times 10^{-3}\ L\ mol^{-1}$, [$BCl_3$] = 0.053 mol L^{-1}, and [TMeStCl] = 0.001 mol L^{-1}, [$P_n^+BCl_4^-$] = 1.22×10^{-7} mol L^{-1} was calculated. Using k_p^{app}, $k_p^{\pm} = 1.35 \times 10^4\ L\ mol^{-1}\ s^{-1}$ was obtained at −70 °C. Similarly, $k_p^{\pm}$ was calculated for all other temperatures and these values are presented in Table 1.

The k_p^{app} increases with decreasing temperature (Table 1). Figure 6 shows the Arrhenius plot, ln(k_p^{app}) vs 1/T. From the slope of the Arrhenius plot, the apparent activation energy, E_a, was calculated to be −5.9 kJ mol^{-1}. Negative E_a has already been observed in the living cationic polymerization of α-methylstyrene,[11] styrene,[3] IB,[12] and indene.[13] For TMeSt the negative E_a is the product of two contending effects of temperature; ionization and propagation. Table 1 shows that $k_p^{\pm}$ increases with increasing temperature. From the Arrhenius plot, ln($k_p^{\pm}$) vs 1/T (Figure 7) the activation energy of propagation, E_a^p, was calculated to be 9.0 kJ mol^{-1}. On the other hand K_i decreases with increasing temperature, as shown in Table 1, and thus the negative E_a is due to a larger decrease in the active chain end concentration with increasing temperature compared to the corresponding increase in $k_p^{\pm}$.

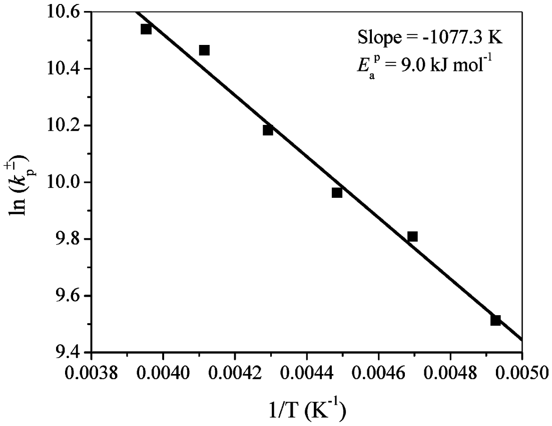

Figure 7. Arrhenius plot of the propagation rate constant for ion pairs to determine the activation energy of propagation, E_a^p.

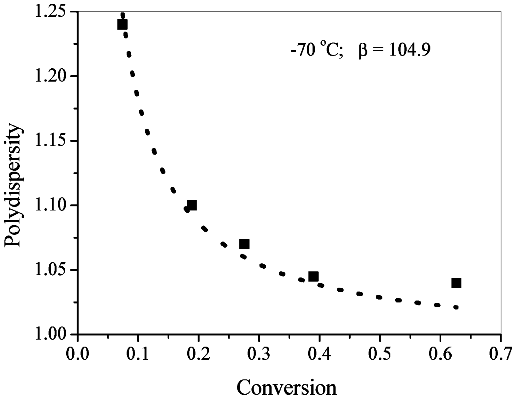

Figure 8. Polydispersity vs conversion curve for the polymerization of TMeSt at −70 °C in CH_2Cl_2; [DTBP] = 0.003 mol L^{-1}, [TMeSt] = 0.136 mol L^{-1}, [TMeStCl] = 0.001 mol L^{-1}, and [BCl_3] = 0.053 mol L^{-1}.

The rate constant of ionization (k_i) and deactivation (k_{-i}) have also been determined, these values are also shown in Table 1. The k_{-i} can be determined from the polydispersity vs conversion (x) plot by curve fitting to eq 4 derived by Müller et al.[14]

$$\bar{M}_w/\bar{M}_n = 1 + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \qquad (4)$$

$\bar{M}_w/\bar{M}_n$ is the polydispersity index and β value is related to k_{-i}, $k_p^{\pm}$ and the initiator concentration $[\mathrm{TMeStCl}]_0$ by $k_{-i} = k_p^{\pm}\beta[\mathrm{TMeStCl}]_0$. Equation 4 is valid when the fraction of active chain end $[P_n^+BCl_4^-]/[\mathrm{TMeStCl}]_0$ is $\leq 10^{-2}$ and $\beta \leq 10$. For the living cationic polymerization of TMeSt in CH_2Cl_2, at all temperatures $[P_n^+BCl_4^-]/[\mathrm{TMeStCl}]_0$ is $\leq 10^{-2}$. The β values at all temperatures, given in Table 1, were determined from the polydispersity vs conversion plot, by curve fitting. The polydispersity vs conversion plot for the living cationic polymerization of TMeSt in CH_2Cl_2 at −70 °C is shown in Figure 8. The k_{-i} values were determined from the β value and $k_p^{\pm}$ at the corresponding temperature. From the K_i and k_{-i} the values of k_i were also calculated and presented in Table 1. As observed before for IB and styrene, the ratio of $k_p^{\pm}/k_{-i}$ decreases with increasing temperature, i.e., propagation is 9.5 times faster than deactivation at −70 °C whereas on average 5.4 monomer units are added during an active cycle at −20 °C. This

Table 2. Thermodynamic Parameters of the Ionization Process

K_i		k_{-i}	
$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta H^{°‡}$ (kJ mol^{-1})	$\Delta S^{°‡}$ (J mol^{-1} K^{-1})
−14.8	−124	11.8	−123

is due to the larger increase of k_{-i} than $k_p^{\pm}$. The increasing k_{-i} value with increasing temperature determines the temperature dependence of K_i and the active center concentration, since the effect of temperature on k_i is negligible.

From the temperature dependence of the ionization process thermodynamic parameters for the living cationic polymerization of TMeSt in CH_2Cl_2 ($\Delta H°$, $\Delta S°$, $\Delta H^{°‡}$ and $\Delta S^{°‡}$) can be calculated according to the following equations

$$\frac{\Delta H°}{RT} - \frac{\Delta S°}{R} = -\ln K_i \qquad (5)$$

$$\mathrm{k} = \frac{\kappa T}{h}\exp\left(-\frac{\Delta H^{0‡}}{RT}\right)\exp\left(\frac{\Delta S^{0‡}}{R}\right) \qquad (6)$$

where k = rate constant, κ = Boltzmann constant, and h = Planck's constant. The plot of $\ln K_i$ vs $1/T$ was used to determine $\Delta H°$ and $\Delta S°$ for the ionization process. From the Eyring plot of $\ln(k_{-i}/T)$ vs $1/T$, the standard enthalpy of activation ($\Delta H^{°‡}$) and the standard entropy of activation ($\Delta S^{°‡}$) for the ionization process were calculated. The results, summarized in Table 2, show that the ionization process is exothermic and exoentropic. The negative $\Delta H°$ for the equilibrium constant of ionization means that at lower temperature, the extent of ionization is higher. The enthalpy of activation for deactivation is positive as expected. The magnitude of activation entropy[15] and overall entropy change for second-order reactions between two molecules, A and B is determined by (a) restriction of translational and rotational motion when A and B are brought together results in a negative $\Delta S^{0‡}$, (b) reorganization of the solvent molecules surrounding the reactants when A and B are brought together results in a positive $\Delta S^{0‡}$, and (c) other properties specific to A and B and the nature of the resulting transition state may result in either positive or negative $\Delta S^{0‡}$. The combined effects in this case yield moderate negative $\Delta S^{0‡}$ values for ionization and deactivation.

Determination of Propagation Rate Constant by Competition Experiment. Competition experiments are especially useful to determine the rate constant of propagation when the active chain end concentration cannot be determined directly from spectroscopic studies due to the absence of UV−visible absorbance or when the concentration of cations is extremely low. In competition experiments, i.e., polymerizations carried out in the presence of a suitable trapping/terminating agent, conversion and the number-average degree of polymerization ($DP_{n\infty}$) reach a limiting value. This technique has been successfully used to determine $k_p^{\pm}$ for IB[1−2,16] and St.[3] The reactivity ratio ($k_p^{\pm}/k_c^{\pm}$) can be calculated from $DP_{n\infty}$, shown for TMeSt in eq 7, or from the limiting conversion using a separate equation.

$$\frac{\mathrm{k_p}^{\pm}}{\mathrm{k_c}^{\pm}} = \frac{\ln(1 - \mathrm{DP}_{n\infty}[\mathrm{TMeStCl}]_o/[\mathrm{TMeSt}]_o)}{\ln(1 - [\mathrm{TMeStCl}]_o/[\pi\mathrm{Nu}]_o)} \qquad (7)$$

Scheme 1. Reaction of I and II with 2-Chloropropene in the Presence of Strong Lewis Acids in CH_2Cl_2

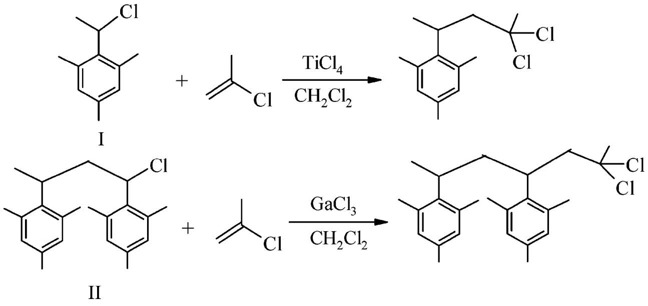

Table 3. Competition Experiment of TMeSt with 2-Chloropropene Capping Agent in CH_2Cl_2 at −70 °C[a]

convn (%)	M_n	$M_{n,cal}$	PDI	$k_p^{\pm}/k_c^{\pm}$	$k_p^{\pm}$ (M_n) (L mol^{-1} s^{-1})
48.6	2600 (GPC) 2800 (^{1}H NMR) 2900 (^{13}C NMR) 2700 (EA)	3550	1.7	1339	8.3×10^4

[a] [TMeStCl] = 0.001 mol L^{-1}, [DTBP] = 0.003 mol L^{-1}, [TMeSt] = 0.05 mol L^{-1}, [BCl_3] = 0.053 mol L^{-1}, and [2-chloropropene] = 3 mol L^{-1}.

In eq 7, $[\mathrm{TMeStCl}]_0$ is the initial concentration of the chain ends, $[\pi\mathrm{Nu}]_0$ is the initial π-nucleophile concentration and $[\mathrm{TMeSt}]_0$ is the initial concentration of the monomer. Using eq 7 $k_p^{\pm}$ can be calculated if $k_c^{\pm}$ is known. In the diffusion clock method, used for IB and St, a trapping agent is selected which reacts with the propagating cation at a diffusion limited rate. The diffusion clock method, however, can only be applied when $k_p^{\pm}$ is not very much lower than 3×10^9 L mol^{-1} s^{-1}. If capping is many orders of magnitude faster than propagation, polymerization will be virtually absent. It is obvious that the diffusion clock method cannot be used in the polymerization of TMeSt. However, eq 7 is also valid when a capping agent, which adds to the chain end at a much lower rate, is employed. In this case, however, $k_c^{\pm}$ must be determined separately. It has been shown that 2-chloropropene, a weak π-nucleophile[4b] adds to TMeSt carbocations, which is followed by a very rapid ion-collapse (Scheme 1).[10] For the addition reactions of 2-chloropropene to the mesitylethyl cation (**I**$^+$) and the corresponding dimer (**II**$^+$) in CH_2Cl_2 at −70 °C $k_c^{\pm}$ = 24.0 L mol^{-1} s^{-1} and 62.0 L mol^{-1} s^{-1} have been determined from the Eyring activation parameters.[9]

Since the $k_c^{\pm}$ for the addition reaction of 2-chloropropene to the **I**$^+$ or **II**$^+$ carbocations in CH_2Cl_2 at −70 °C are known, polymerization of TMeSt was carried out in the presence of 2-chloropropene with BCl_3 as co-initiator at −70 °C in CH_2Cl_2 solvent and DTBP as proton trap. Limiting conversion was reached in less than 15 min. The results are shown in Table 3. The ^{1}H NMR spectrum shows the presence of the $-CH_2-CCl_2-CH_3$ chain end (at ~3 ppm). In the ^{13}C NMR spectrum (Figure 9), the peaks at ~92 and ~58 ppm respectively confirm the presence of $-CCl_2$ and $-CH_2-$ groups as chain end. The resonance signals of poly(2,4,6-trimethylstyrene) are closely similar to those observed for the adducts in Scheme 1.[9] The number-average molecular weight was determined by GPC, ^{1}H NMR and inverse gated ^{13}C NMR spectroscopy and elemental analysis (EA) [C, 87.00%; H, 9.44%; Cl, 2.63%]. The M_n of the polymer calculated by NMR spectroscopy and EA assuming one 2-chloropropene moiety per chain was in

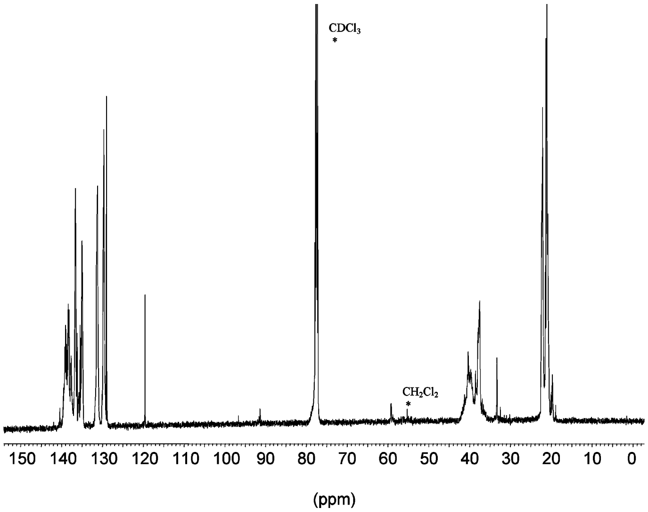

Figure 9. ^{13}C NMR spectrum of poly(2,4,6-trimethylstyrene) obtained after the polymerization of TMeSt in the presence of 2-chloropropene as a π-nucleophile.

good agreement with that determined by GPC, suggesting complete capping of the polymeric cation and the absence of side reactions such as proton elimination. The molecular weight distributions of the polymers were close to the expected most probable distribution ($M_w/M_n \approx 2$).

Competition experiments were also carried out in the absence of initiator. After 15 min 3.1% conversion was obtained, which confirms that direct initiation is operational in the competition experiments with 2-chloropropene but is much slower than capping so that the kinetics of capping is not affected. If carbocation **II**$^+$ is accepted as a model for the propagating cation in the polymerization of TMeSt, using $k_c^{\pm} = 62$ L mol^{-1} s^{-1} $k_p^{\pm} = 8.3 \times 10^4$ L mol^{-1} s^{-1} was calculated from eq 7. This value is similar to that obtained from directly determined cation concentration and the apparent rate constant of propagation confirming the general applicability of the competition method.

Conclusions

The carbocationic polymerization of 2,4,6-trimethylstyrene initiated by the 1-chloro-1-(2,4,6-trimethylphenyl)ethane/BCl$_3$ initiating system in CH$_2$Cl$_2$ proceeds in a living fashion without side reactions in the temperature range of −70 to −20 °C. The absolute rate constant of propagation for ion pairs could be determined from both UV−visible spectroscopy and competition experiments. The $k_p^{\pm}$ values obtained from the two methods are similar, which confirms the general applicability of the competition experiments for the determination of absolute rate constants of propagation in carbocationic polymerization. The $k_p^{\pm}$ values increases slightly with increasing temperature with an activation energy of propagation = 9.0 kJ mol^{-1}. The overall polymerization rate, however, decreases with increasing temperature due to a larger decrease in the active center concentration, and the apparent activation energy of polymerization is negative, −5.9 kJ mol^{-1}. The $k_p^{\pm}$(20 °C) = 6.7 × 10^4 L mol^{-1} s^{-1} extrapolated for 20 °C is much lower than the 3 × 10^7 L mol^{-1} s^{-1} predicted by the linear free energy relationship described in the preceding article.[9] Since these linear free energy correlations do not specifically treat steric effects, the deviation may predominantly be due to the bulkiness of the propagating carbocation in 2,4,6-trimethylstyrene polymerization, as explained in the preceding article.[9]

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