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Determination of Rate Constants in the Carbocationic Polymerization of Styrene: Effect of Temperature, Solvent Polarity, and Lewis Acid[1]

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ABSTRACT: The electrophilicity parameter ($E = 9.6$) of the 1-phenylethyl cation, $\mathbf{1}^+$, has been determined and combined with the nucleophilicity parameter ($N = 0.78$, $s = 0.95$) of styrene (St) to predict diffusion-limited propagation in the cationic polymerization of St by the linear free energy relationship $\log k = s(N + E)$. This prediction has been experimentally verified using two different diffusion clock methods, which provided a value of $k_p^{\pm} \approx 2 \times 10^9$ L mol^{-1} s^{-1}, 6 orders of magnitude higher than previously accepted, for the absolute rate constant of propagation of the $TiCl_4$-induced polymerization of St in methylcyclohexane/methyl chloride 60/40 (v/v) at −80 °C. The $k_p^{\pm}$ value remained unchanged in the temperature range −50 to −80 °C, indicating that propagation does not have an enthalpic barrier; however, it increased moderately with increasing solvent polarity. The nature of the Lewis acid has little effect on $k_p^{\pm}$ as similar values have been obtained with $TiCl_4$ or $SnCl_4$. The apparent rate constant of ionization, k_i^{app}, the rate constant of deactivation, k_{-i}, and the apparent equilibrium constant of ionization, K_i^{app}, have also been determined as a function of temperature. The k_i^{app} increases slightly and k_{-i} increases moderately with increasing temperature; therefore, K_i^{app} and the overall polymerization rate decrease moderately with increasing temperature.

Introduction

Polymerization kinetics is one of the most important but still unsolved issues in carbocationic polymerization. Our problems to determine elementary rate constants, particularly the rate constant of propagation (k_p), may be attributed to difficulties involved in the accurate determination of the active center concentration.[2−5] In the case of styrene (St), UV spectroscopy can be used to measure the cation concentration, and several groups have attempted to determine k_p.[3] Pepper's group used the stopped-flow technique for the first time in 1974 to monitor the perchloric acid-induced polymerization of St in CH_2Cl_2 over a temperature range of 0 to −97 °C and reported k_p values in the range 10^4−10^3 L mol^{-1} s^{-1}.[6] In 1979, Kunitake and Takarabe reported studies on the CF_3SO_3H-initiated polymerization of St in CH_2Cl_2 using stopped-flow and rapid quenching techniques over the temperature range 30 to −1 °C and reported k_p values in the order of 10^5−10^4 L mol^{-1} s^{-1}.[7] More recently, Vairon's group used a specially designed stopped-flow apparatus and reported k_ps from $\sim 10^5$ to 10^3 L mol^{-1} s^{-1} in the temperature range −10 to −62 °C.[8] In a preliminary study, we investigated the addition reaction of 1,1-di-*p*-tolylethylene (DTE) to dimeric styryl living ends in conjunction with $TiCl_4$ in $CHCl_3$/CH_2Cl_2 70/30 (v/v) at −75 °C.[9] Assuming diffusion-limited addition of DTE to polystyryl cation, we calculated the propagation rate constant for ion pairs, $k_p^{\pm} = 5 \times 10^9$ L mol^{-1} s^{-1}, i.e., diffusion-limited propagation for the polymerization of St. This value is 6 orders of magnitude higher than that reported by the stopped-flow method and prompted us to carry out a detailed kinetic study of the cationic polymerization of St.

Non(homo)polymerizable monomers such as 1,1-diphenylethylene (DPE), DTE, 1,1-di(4-*tert*-butylphenyl)ethylene (DBE), and 2-phenylfuran (2-PhFu) have been invaluable for the synthesis of end-functionalized polymers and block copolymers by carbocationic polymerization.[10] The key requirement in this process is a quantitative monoaddition of non(homo)polymerizable monomers to the living cationic end, yielding stable and fully ionized chain ends. In addition to the utility of non(homo)polymerizable π-nucleophiles in polymer synthesis, we have recently introduced two different diffusion clock methods to determine k_ps based on diffusion-limited addition of some π-nucleophiles.[11] The first method involves on-line UV−vis monitoring of the addition of non(homo)polymerizable π-nucleophiles, which add at diffusion-limited rate. This allows the determination of the apparent equilibrium constant of ionization (K_i^{app}) and thus the concentration of active chain ends. With the knowledge of the cation concentration and the rate of polymerization, k_p can be calculated. The second simple diffusion clock method involves competition experiments, i.e., polymerization carried out in the presence of a π-nucleophile, which stops short of completion when all chain ends are capped. From the limiting conversions or number-average degrees of polymerization, k_p can be obtained. Since both methods are carried out under conditions where the dissociation of ion pairs to free ions is suppressed, both techniques yield the propagation rate constants for ion pairs ($k_p^{\pm}$). For the polymerization of isobutylene in hexanes/methyl chloride (MeCl) 60/40 (v/v) at −80 °C in conjunction with $TiCl_4$ in the presence of 2,6-di-*tert*-butylpyridine (DTBP), both methods yielded similar $k_p^{\pm}$ values ranging from 0.3×10^9 to 1.0×10^9 L mol^{-1} s^{-1}, 4 orders of magnitude

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higher than previously accepted values. Plesch attempted to explain this large discrepancy in a recent paper[4] by proposing first-order propagation on monomer complexed cations at high monomer concentration and second-order propagation at monomer concentrations close to zero. This explanation, however, is not convincing, as pointed out by Sigwalt,[5] who proposed another interpretation involving a two-step propagation. The first step is the formation of monomer solvated cations, which subsequently add monomer. It is clearly apparent from these papers that the absolute rate constants of propagation in carbocationic polymerization will remain a subject of discussion until an agreement is reached.

We now extend our original investigation with isobutylene[11] to styrene. In this study, the kinetics and mechanism of capping of 1-phenylethyl cation (**1**$^+$) with DTE and 2-PhFu were studied at different temperature using on-line UV−vis spectroscopy. Competition experiments were also carried out to investigate the effect of temperature, solvent polarity, and nature of Lewis acid on the absolute propagation rate constant of the carbocationic polymerization of St. The experimentally determined value is compared to that predicted by the linear free energy relationship.

Experimental Section

Materials. Styrene (St, Aldrich, 99%) and *p*-methylstyrene (*p*-MeSt, Aldrich, 97%) were freed from inhibitor by washing with 5% NaOH and then repeatedly with water. After drying overnight over anhydrous Na_2SO_4, they were distilled from calcium hydride under reduced pressure. The 1-chloro-1-(4-methylphenyl)ethane (*p*-MeStCl),[12] 2-phenylfuran (2-PhFu),[13] and 1,1-di-*p*-tolylethylene (DTE)[14,15] were synthesized according to the literature. All other chemicals and solvents were purified as described previously or used as received.[11]

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^{-1}. The measurements were carried out at room temperature. The molecular weights and molecular weight distributions (PDI) were determined using the universal calibration curve and Viscotek TriSEC GPC software. The ^{1}H and ^{13}C NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane as internal standard (δ_H 0.00) or to the solvent signal (δ_C 77.0), respectively. DEPT-135 experiments were used to obtain information about the multiplicities of ^{13}C NMR resonances.

Synthesis of 1-Chloro-1-phenylethane (1-Cl). In Lowell, **1-Cl** was synthesized by hydrochlorination of St in CH_2Cl_2 (1:3 v/v) at 0 °C. In München **1-Cl** was synthesized by reaction of thionyl chloride (0.25 mol) with 1-phenylethanol (0.20 mol) in CH_2Cl_2 (100 mL, room temperature, 86% yield); bp 95−100 °C/10 mbar (bp 85 °C/20 Torr).[16] The ^{1}H NMR chemical shifts ($CDCl_3$) were in accord with those given in ref 15.

1-Chloro-1,3-diphenylbutane (4-Cl) was obtained from St and **1-Cl** in the presence of a zinc chloride−etherate catalyst as a mixture of diastereomers by following a procedure described in ref 17.

Synthesis of 2-Methyl-4-phenyl-1-pentene (3a). A solution of $TiCl_4$ (0.50 mL, 4.6 mmol) and DTBP (5 μL) in dichloromethane (15 mL) was cooled to −78 °C. Then a mixture of **1-Cl** (422 mg, 3.00 mmol) and (2-methylallyl)trimethylsilane (**2a**, 2.31 g, 18.0 mmol) in dichloromethane (2 mL) was added dropwise. After stirring at −78 °C for 2 h, the solution was alkalized with concentrated NH_3/water (20 mL, 1/1) and filtered through Celite. The layers were separated, and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in a vacuum. Bulb-to-bulb distillation gave **3a** (0.47 g, 98%) as a colorless oil; bp 20 °C/0.007 mbar. ^{1}H and ^{13}C NMR chemical shifts were identical with those reported in ref 18. MS (EI, 70 eV) *m*/*z* (%): 160 (M$^+$, 8), 105 (100), 77 (10).

Synthesis of 4-Phenyl-1-pentene (3b). A solution of $TiCl_4$ (0.75 mL, 6.8 mmol) in dichloromethane (15 mL) was cooled to −78 °C. Then a mixture of **1-Cl** (703 mg, 5.00 mmol) and allyltrimethylsilane (**2b**, 1.14 g, 10.0 mmol) in dichloromethane (2 mL) was added dropwise. After stirring at −78 °C for 2 h, the solution was alkalized with concentrated NH_3/water (20 mL, 1/1) and filtered through Celite. The layers were separated, and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in a vacuum. Bulb-to-bulb distillation gave **3b** (0.60 g, 82%) as a colorless oil; bp 20 °C/0.005 mbar. ^{1}H NMR (300 MHz, $CDCl_3$) and MS (EI, 70 eV) spectral data were identical with those reported in ref 18. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.5 (q, C-5), 39.7 (d, C-4), 42.7 (t, C-3), 115.9 (t, C-1), 126.0, 127.0, 128.3 (3 d, Ph), 137.1 (d, C-2), 147.0 (s, Ph).

Synthesis of 2-Methyl-4,6-diphenyl-1-heptene (5a). A solution of $TiCl_4$ (948 mg, 5.00 mmol) and DTBP (10 μL) in dichloromethane (45 mL) was cooled to −78 °C. Then a mixture of **4-Cl** (300 mg, 1.23 mmol) and **2a** (316 mg, 2.46 mmol) in dichloromethane (5 mL) was added dropwise. After stirring at −78 °C for 2 h, the solution was alkalized with concentrated NH_3/water (50 mL, 1/1) and filtered through Celite. The layers were separated, and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in a vacuum. Bulb-to-bulb distillation gave **5a** (0.18 g, 55%) as a colorless oil; bp 190−200 °C (oven temperature)/0.08 mbar. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12−2.81 (m, 12 H), 4.55, 4.65 (2 m$_c$, 2 × 1 H, 1-H), 7.06−7.33 (m, 10 H, Ph); MS (EI, 70 eV) *m*/*z* (%): 264 (M$^+$, 4), 105 (100), 91 (19), 77 (15).

Synthesis of 4,6-Diphenyl-1-heptene (5b). A solution of $TiCl_4$ (948 mg, 5.00 mmol) in dichloromethane (45 mL) was cooled to −78 °C. Then a mixture of **4-Cl** (734 mg, 3.00 mmol) and **2b** (686 mg, 6.00 mmol) in dichloromethane (5 mL) was added dropwise. After stirring at −78 °C for 2 h, the solution was alkalized with concentrated NH_3/water (50 mL, 1/1) and filtered through Celite. The layers were separated, and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in a vacuum. Bulb-to-bulb distillation gave **5b** (0.44 g, 59%) as a mixture of diastereomers; bp 160−170 °C (oven temperature)/0.01 mbar. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13, 1.20 (2 d, each J = 6.9 Hz, 3 H, 7-H), 1.82−2.00 (m, 2 H), 2.23−2.70 (m, 4 H), 4.84−4.95 (m, 2 H, 1-H), 5.45−5.69 (m, 1 H, 2-H), 7.01−7.30 (m, 10 H, Ph). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.0, 23.9 (2 q, C-7), 36.8, 37.4 (2 d, C-6), 41.5, 42.0 (2 t, C-5), 43.2, 43.4 (2 d, C-4), 44.0, 44.7 (2 t, C-3), 115.8, 119 (2 t, C-1), 125.8, 125.9, 126.0, 126.1, 126.4, 126.8, 127.3, 127.6, 127.9, 128.0, 128.2, 128.3 (12 d, Ph), 136.8 (d, C-2), 144.8, 145.0, 146.8, 148.0 (4 s, Ph). MS (EI, 70 eV) *m*/*z* (%): 250 (M$^+$, 4), 106 (11), 105 (100), 91 (19), 77 (10).

Synthesis of 1,3-Diphenylbutane (5c). A solution of $TiCl_4$ (948 mg, 5.00 mmol) in dichloromethane (30 mL) was cooled to −78 °C. Then a mixture of **4-Cl** (734 mg, 3.00 mmol) and **2c** (781 mg, 3.00 mmol) in dichloromethane (5 mL) was added dropwise. After stirring at −78 °C for 2 h, the solution was alkalized with concentrated NH_3/water (50 mL, 1/1) and filtered through Celite. The layers were separated, and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in a vacuum. Bulb-to-bulb distillation gave **5c** (0.32 g, 51%) as a colorless oil; bp 160−170 °C (oven temperature)/0.07 mbar. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (d, J = 7.0 Hz, 3 H, 4-H), 1.88−1.95 (m, 2 H, 2-H), 2.45−2.53 (m, 2 H, 1-H), 2.60−2.76 (m, 1 H, 3-H), 7.10−7.30 (m, 10 H, Ph). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 22.7 (q, C-4), 34.1 (t, C-1), 39.7 (d, C-3), 40.2 (t, C-2), 125.8, 126.1, 127.3, 128.4, 128.6 (5 d, Ph), 142.7, 147.5 (2 s, Ph).

Competition Experiments. Relative Reactivities of 2a and 2b toward the Cation 1$^+$. Under an atmosphere of dry nitrogen, a mixture of **1-Cl**, **2a**, and **2b** was dissolved in dry dichloromethane (20 mL), polymer-bound DTBP (ca. 5 mg) was added, and the solution was cooled to −78 °C. Subsequently, the reaction was started by adding $TiCl_4$. After stirring at −78 °C for 60 min, the reaction mixture was hydrolyzed with concentrated NH_3/water (10 mL, 1/1). The organic layer was separated, dried over $MgSO_4$, filtered, and analyzed by GC (Perkin-Elmer Sigma 3, packed column SE 30, 2.5 m × 4 mm).

Relative Reactivities of 2a and 2c toward the Cation 1^+. Under an atmosphere of dry nitrogen, a mixture of **1-Cl**, **2a**, and **2c** was dissolved in dry dichloromethane (5 mL), a drop of DTBP was added, and the solution was cooled to −78 °C. Subsequently, the reaction was started by adding a solution of $TiCl_4$ in dry dichloromethane. After stirring at −78 °C for 75 min, the reaction mixture was hydrolyzed with concentrated NH_3/water (10 mL, 1/1). The organic layer was separated, dried over $MgSO_4$, filtered, and analyzed by GC (Perkin-Elmer Sigma 3, packed column SE 30, 2.5 m × 2 mm). The relative reactivities[19] of **2a**/**2d** mixtures toward $\mathbf{1}^+$ and of **2a**/**2b** and **2a**/**2c** mixtures toward $\mathbf{4}^+$ were determined in analogy to the procedure given above.

Details of the competition experiments are described in the Supporting Information.

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. Throughout the study St was considered as an apolar solvent, and its volume was added to the volume of methylcyclohexane (MeCHx). The total volume of the reaction mixture was 20 mL. After predetermined time polymerization was terminated by the addition of excess prechilled methanol (0.5 mL). 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 DTE or 2-PhFu as a π-nucleophile. In a typical competition experiment the polymerization was carried out in MeCHx/MeCl 60/40 (v/v) at −80 °C using the following concentrations: [*p*-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [2-PhFu] = 0.003 mol L^{-1}, [St] = 0.2 mol L^{-1}, and $[TiCl_4]$ = 0.036 mol L^{-1}. Into a 75 mL culture tube at −80 °C 9.2 mL of MeCHx at room temperature, 6.9 mL of MeCl at −80 °C, 0.8 mL of DTBP stock solution in MeCHx (0.1 mol L^{-1}) at −80 °C, 0.8 mL of *p*-MeStCl stock solution in MeCHx (0.05 mol L^{-1}) at −80 °C, 0.46 mL of St at room temperature, and 2.0 mL of 2-PhFu stock solution in MeCHx/MeCl 60/40 (v/v) at −80 °C (0.03 mol L^{-1}) were added and mixed thoroughly. The polymerization was started by the addition of 0.8 mL of $TiCl_4$ solution (0.9 mol L^{-1}, in MeCHx/MeCl 60/40 (v/v)) at −80 °C. After predetermined time (2 h) 0.5 mL of prechilled methanol was added to the reaction mixture to quench the polymerization. The polymer was precipitated twice from methanol to obtain 153.3 mg of polymer (conversion = 36.8%, $M_n = 3920$, PDI = 1.8).

UV−Vis Spectroscopy. UV−vis spectroscopic measurements were carried out under a dry nitrogen atmosphere ($[H_2O] < 0.5$ ppm) in a glovebox. A quartz immersion probe (661.300-QX, Hellma, optical path 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).

The solution of **1-Cl**, DTBP, and $TiCl_4$ in MeCHx/MeCl 60/40 (v/v) solvent was kept at −80 °C for about 1 h, allowing complex inorganic salts to precipitate. Then, the solution was filtered at −80 °C in the glovebox by using a vacuum pump, and the reference spectrum was taken. The π-nucleophile stock solution was added under stirring, and the visible spectroscopic measurement was started. For the calculation of the apparent rate constant of the capping reaction, the concentration of St-DTE^+ or St-2-$PhFu^+$ carbenium ions was derived from the measured absorbance at the absorption maximum $\lambda_{max} = 465$ and 335 nm and the corresponding molar absorption coefficient $\epsilon_{max} = 44\,000$ and $30\,000$ L mol^{-1} cm^{-1}, respectively, for DTE and 2-PhFu and path length $d = 0.02$ cm.

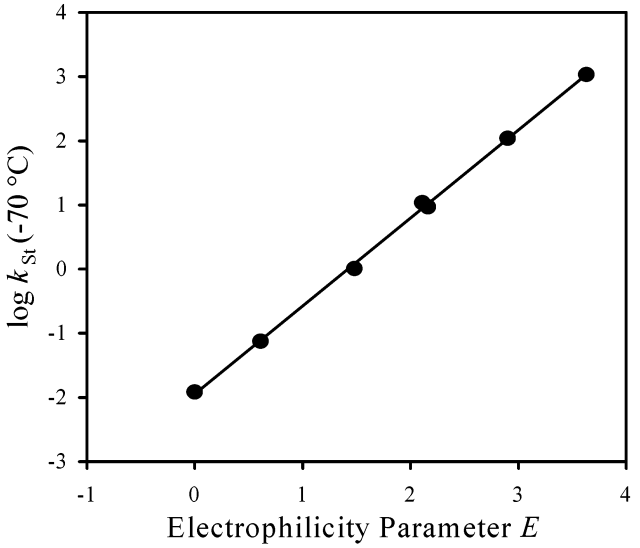


Figure 1. Correlation log k_{St}(Ar_2CH^+ + styrene, −70 °C, from ref 27) with the empirical electrophilicity parameters E of Ar_2CH^+ (from refs 21 and 22).

Results and Discussion

Estimation of the Propagation Rate Constants of Styrene: The Organic Chemist's Approach. The rates of reactions of carbocations with alkenes and other types of nucleophiles can generally be described by the linear free energy relationship (LFER), eq 1,[20−25] where E is an electrophilicity parameter, N is a nucleophilicity parameter, and s is a nucleophile-specific slope parameter which is usually close to 1 and can be neglected in semiquantitative treatments of reactivity.

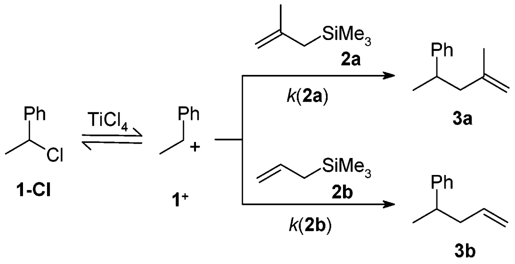
$$\log k_{20°C} = s(N + E) \qquad (1)$$

This equation reproduces rate constants $k_{20°C} < 10^8$ L mol^{-1} s^{-1} with an accuracy of better than a factor of 10−100.[21−25] Rate constants $k_{20°C} > 10^8$ L mol^{-1} s^{-1} are generally calculated too high because eq 1 does not take into account the flattenings of the log k vs E correlations which occur as the diffusion limit is approached.[22,26]

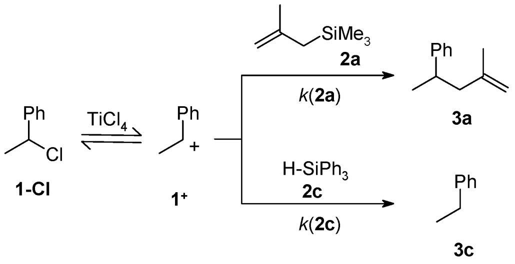
Investigation of numerous reactions of benzhydrylium ions with St[27] gave the reactivity parameters $N = 0.78$ and $s = 0.95$ for St.[21] Because of the high quality of the log k_{St} vs E correlation of the reactions of St with benzhydrylium ions (Figure 1), St has recently been selected as a reference nucleophile and is recommended as a probe for the quantitative determination of the electrophilicities of carbocations.[21,22] To derive the propagation rate constants of St, the electrophilicity parameter of the polystyryl cation is needed in addition.

McClelland and co-workers recently reported a rate constant of $k > 5 \times 10^7$ s^{-1} for the reaction of the 1-phenylethyl cation $\mathbf{1}^+$ with trifluoroethanol at 20 °C.[28] With the reactivity parameters $N = 1.23$ and $s = 0.92$ for trifluoroethanol,[29] one can derive a lower limit for the electrophilicity parameter for carbocation $\mathbf{1}^+$ ($E > 7$). We have now determined the electrophilicity of the 1-phenylethyl cation $\mathbf{1}^+$ more precisely. Because of its high reactivity, we have not performed direct rate measurements but instead employed a diffusion clock method.[11,26,30]

Scheme 1



Scheme 2



When a mixture of **1-Cl** with an excess of the allylsilanes **2a** and **2b** was treated with $TiCl_4$ in dichloromethane at −78 °C, the product ratio **3a**/**3b** determined by GC indicated **2a** to be 1.4 times more reactive than **2b** (Scheme 1). Because direct rate measurements as well as competition experiments have consistently shown that **2a** is approximately 10^3 times more reactive than **2b** in reactions with a variety of less electrophilic carbocations,[21,22] the observed reactivity ratio of $k(\mathbf{2a})/k(\mathbf{2b}) = 1.4$ is clear evidence for the diffusion-controlled reaction of the 1-phenylethyl cation $\mathbf{1}^+$ with **2a**.

In a second competition experiment (Scheme 2) 2-methylallyltrimethylsilane **2a** was 37 times more reactive toward the 1-phenylethyl cation $\mathbf{1}^+$ than triphenylsilane **2c**.

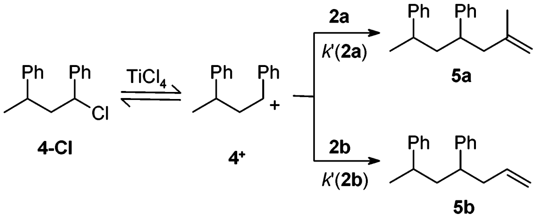
With the assumption of $k(\mathbf{2a}) = 3 \times 10^9$ L mol^{-1} s^{-1} (diffusion control)[31] one derives $k(\mathbf{2c}) = 8 \times 10^7$ L mol^{-1} s^{-1}. This calculation combines rate constants determined at 20 °C with relative rates at −78 °C. This procedure is generally allowed for fast bimolecular reactions which proceed with an activation energy of zero.[32,33]

As the rate constant $k(\mathbf{2c})$ thus determined is within the validity of eq 1, one can now use the published reactivity parameters of **2c** ($N = 2.06$ and $s = 0.68$)[21] to calculate $E(\mathbf{1}^+) = 9.6$. An analogous competition experiment, where triphenylsilane (**2c**) in Scheme 2 was replaced by dimethylphenylsilane (**2d**, $N = 3.27$ and $s = 0.73$)[21] gave $k(\mathbf{2a})/k(\mathbf{2d}) = 3.9$ and $k(\mathbf{2d}) = 8 \times 10^8$ L mol^{-1} s^{-1}. This value is outside the validity of eq 1 and cannot be employed for calculating $E(\mathbf{1}^+)$.

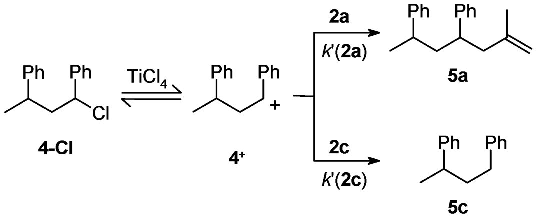
Because the reactivity of cation $\mathbf{4}^+$ has been suggested to differ considerably from that of $\mathbf{1}^+$,[28] an analogous set of competition experiments have been performed with the hydrochloride of the styrene dimer (**4**-Cl). From the product ratio **5a**/**5b** obtained in the competition experiment depicted in Scheme 3, one can derive a ratio of rate constants $k'(\mathbf{2a})/k'(\mathbf{2b}) = 1.5$. As discussed above, this small ratio is indicative of a diffusion-controlled reaction of $\mathbf{4}^+$ with 2-methylallyltrimethylsilane (**2a**).

A competition experiment analogous to that described in Scheme 2 showed that $\mathbf{4}^+$ reacted 40 times faster with the methylallylsilane **2a** than with the hydride donor **2c** (Scheme 4).

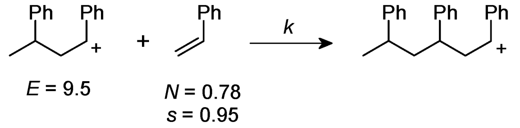
Scheme 3



Scheme 4



Scheme 5



With the same line of arguments, the ratio $k'(\mathbf{2a})/k'(\mathbf{2c}) = 40$ yielded $k'(\mathbf{2c}) = 7.5 \times 10^8$ L mol^{-1} s^{-1} and $E(\mathbf{4}^+) = 9.5$, i.e., almost the same value as for the 1-phenylethyl cation $\mathbf{1}^+$. In contrast to McClelland,[28] we, therefore, do not find evidence for a significant change of electrophilicity from $\mathbf{1}^+$ to $\mathbf{4}^+$.

When the electrophilicity parameters thus determined are combined with the nucleophilicity parameters of St, eq 1 predicts a rate constant of $k = 6 \times 10^9$ L mol^{-1} s^{-1} for the reaction depicted in Scheme 5.

As discussed above, eq 1 does not account for the flattening of log k vs E correlations at $k > 10^8$ L mol^{-1} s^{-1} and, therefore, overestimates the rates of fast reactions. It is obvious, however, from these considerations that the addition rate constant k depicted in Scheme 5 must be on the order of 10^9 L mol^{-1} s^{-1}, in agreement with McClelland's experiments.[28]

The same order of magnitude can be derived from the correlation shown in Figure 2. The directly measured rate constants for the reactions of benzhydrylium ions with St at −70 °C[27] correlate linearly with the directly measured solvolysis rate constants of the corresponding benzhydryl chlorides in 100% ethanol at 25 °C.[34] Extrapolation of this correlation to $\log k_{\mathrm{EtOH}} = -6.78$, the experimental ethanolysis rate constant (25 °C) of **1-Cl**,[35] again predicts a reactivity of $\mathbf{1}^+$ toward St of $k \approx 10^9$ L mol^{-1} s^{-1}, in agreement with the conclusions derived above.

Determination of the Propagation Rate Constants of Styrene: The Polymer Chemist's Approach. UV−vis Spectroscopic Study of the Capping Reaction. In the elucidation of polymerization mechanisms, low molecular weight model compounds resembling the chemical structure of a growing chain end can be employed when their chemical properties are very similar to those of the polymer chain end. In the previous section it was shown that the reactivities of the monomeric and dimeric cations $\mathbf{1}^+$ and $\mathbf{4}^+$ do not differ; thus, the end-capping of $\mathbf{1}^+$ with π-nucleophiles (πNu) DTE and 2-PhFu was studied using hydrochlorinated St (**1-Cl**) as a model compound in conjunction

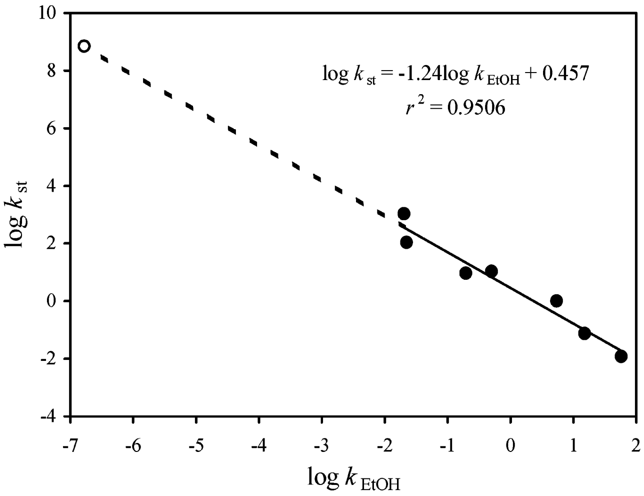
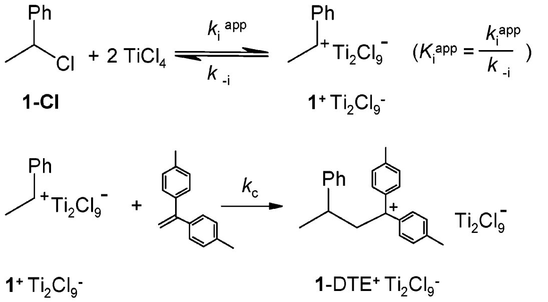


Figure 2. Correlation of the rate constants log k_{St} (Ar_2CH^+ + styrene, −70 °C, from ref 27) with the solvolysis rate constants of Ar_2CH-Cl in 100EtOH (25 °C, from ref 34).

Scheme 6. Ionization Equilibrium and Capping Reaction of 1-Cl with DTE



with $TiCl_4$ in MeCHx/MeCl 60/40 (v/v) solvent mixtures at −80 °C. Scheme 6 describes the capping of **1-Cl** with a πNu, for example with DTE. Capping is a two-step process that involves the ionization of the chain end and subsequent addition of the πNu. According to Scheme 6, the apparent equilibrium constant of ionization (K_i^{app}) of **1-Cl** can be expressed by eq 2.

$$K_i^{app} = \frac{k_i^{app}}{k_{-i}} = \frac{[\mathbf{1}^+Ti_2Cl_9^-]}{[\mathbf{1\text{-}Cl}][TiCl_4]^2} \qquad (2)$$

Under the reaction conditions used in this study, the concentration of free $\mathbf{1}^+$ ions is negligible compared to that of ion pairs in MeCHx/MeCl 60/40 (v/v),[36] and the initial evolution of capped species with time can be expressed by eq 3.

$$\frac{d}{dt}([\mathbf{1}\text{-}\pi Nu^+Ti_2Cl_9^-] + [\mathbf{1}\text{-}\pi Nu^+]) = k_c[\mathbf{1}^+Ti_2Cl_9^-][\pi Nu] \qquad (3)$$

The left side of eq 3 contains the sum of the concentrations of capped ion pairs and free ions, which should exhibit the same λ_{max} and ϵ_{max},[37] and therefore the knowledge of the extent of dissociation is not important. In the presence of protonated DTBP salts, however, dissociation is most likely negligible.

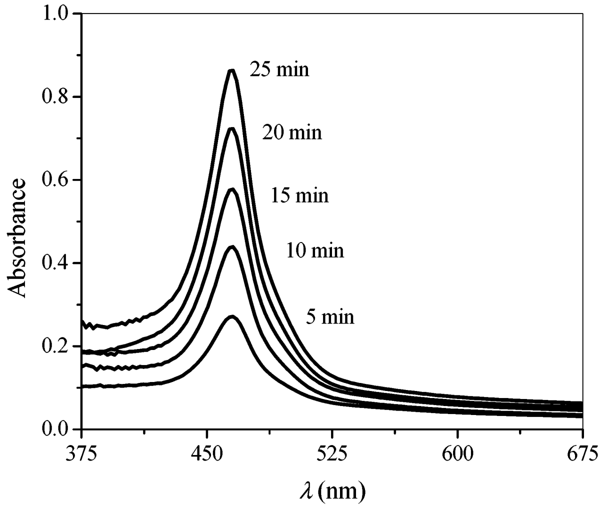


Figure 3. Plots of absorption vs time for the capping reaction of **1-Cl** with DTE; [**1-Cl**] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1}, and [DTE] = 0.00125 mol L^{-1} in MeCHx/MeCl 60/40 (v/v) solvent at − 80 °C.

Assuming steady state for [$\mathbf{1}^+Ti_2Cl_9^-$], i.e.

$$\frac{d}{dt}[\mathbf{1}^+Ti_2Cl_9^-] = k_i^{app}[\mathbf{1\text{-}Cl}][TiCl_4]^2 - k_{-i}[\mathbf{1}^+Ti_2Cl_9^-] - k_c[\mathbf{1}^+Ti_2Cl_9^-][\pi Nu] = 0 \qquad (4)$$

the concentration of $\mathbf{1}^+Ti_2Cl_9^-$ is given according to eq 5.

$$[\mathbf{1}^+Ti_2Cl_9^-] = \frac{k_i^{app}[\mathbf{1\text{-}Cl}][TiCl_4]^2}{k_{-i} + k_c[\pi Nu]} \qquad (5)$$

Using eq 5, eq 3 yields eq 6.

$$\frac{d}{dt}([\mathbf{1}\text{-}\pi Nu^+Ti_2Cl_9^-] + [\mathbf{1}\text{-}\pi Nu^+]) = \frac{k_c k_i^{app}[\mathbf{1\text{-}Cl}][TiCl_4]^2[\pi Nu]}{k_{-i} + k_c[\pi Nu]} \qquad (6)$$

There are two limiting conditions depending on the concentration of πNu used for the capping reaction. If $k_{-i} \gg k_c[\pi Nu]$, the second term in the denominator of eq 6 can be neglected, and eq 6 can be written as eq 7a. Thus, the capping reaction should be first order with respect to πNu concentration.

$$\frac{d}{dt}([\mathbf{1}\text{-}\pi Nu^+Ti_2Cl_9^-] + [\mathbf{1}\text{-}\pi Nu^+]) = k_c K_i^{app}[\mathbf{1\text{-}Cl}][TiCl_4]^2[\pi Nu] \qquad (7a)$$

If $k_{-i} \ll k_c[\pi Nu]$, k_{-i} in the denominator of eq 6 can be neglected, and eq 6 can be written as eq 7b. Under these conditions the capping reaction should be independent of πNu concentration.

$$\frac{d}{dt}([\mathbf{1}\text{-}\pi Nu^+Ti_2Cl_9^-] + [\mathbf{1}\text{-}\pi Nu^+]) = k_i^{app}[\mathbf{1\text{-}Cl}][TiCl_4]^2 \qquad (7b)$$

Because of the generation of $\mathbf{1}\text{-}\pi Nu^+$ species absorbing in the UV or visible region, UV−vis spectroscopy was used to monitor the capping reaction. Figure 3 shows selected visible spectra, which were obtained during the course of the capping reaction of **1-Cl** with DTE in

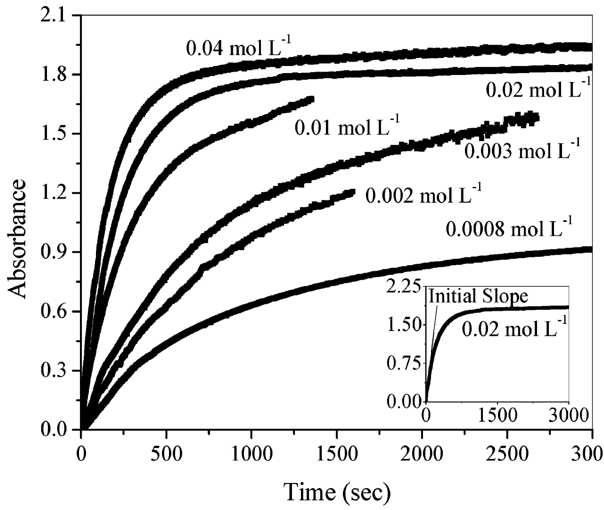


Figure 4. Plot of absorbance at $\lambda_{max} = 465$ nm vs time for the capping reaction of **1-Cl** with different [DTE] in MeCHx/MeCl 60/40 (v/v) at −80 °C. Inset: initial slope at [DTE] = 0.02 mol L^{-1}.

MeCHx/MeCl 60/40 (v/v) solvent at −80 °C. The time-dependent evolution of the absorbance at $\lambda_{max} = 465$ nm is shown in Figure 4. The initial slope (Figure 4) of the absorbance at $\lambda_{max} = 465$ nm vs time plot was used for the calculations. It appears that the concentration of **1**-DTE$^+$ increases until it reaches a plateau, which corresponds to quantitative capping of **1-Cl** with DTE (except when DTE is the limiting reagent).

Quantitative capping of **1-Cl** with DTE was also confirmed by ^{1}H NMR spectroscopy. The absence of unreacted **1-Cl** is supported by the absence of characteristic resonance peaks for $CH_3{-}CH(Ph){-}Cl$, i.e., methine and methyl protons next to chloro group at 5.15 and 1.92 ppm, respectively. The formation of $CH_3{-}CH(Ph){-}CH{=}C(C_6H_4{-}CH_3)_2$ is confirmed from the presence of resonance signals at 1.4, 3.4, and 5.88 ppm for $CH_3{-}$, $-CH(Ph)-$, and $-CH{=}$ protons, respectively.

According to Scheme 6, ionization of **1-Cl** requires two molecules of $TiCl_4$, and thus eq 6 implies that the initial capping rate is proportional to $[TiCl_4]^2$. We have previously reported this behavior in the capping reaction of 2-chloro-2,4,4-trimethylpentane with DPE, DTE, and 2-PhFu in conjunction with $TiCl_4$.[11b] This has been confirmed experimentally in the capping reaction of **1-Cl** with DTE at different $TiCl_4$ concentrations. Figure 5 shows the corresponding bilogarithmic plots of the initial capping rates as a function of [$TiCl_4$], which confirms second-order dependence on [$TiCl_4$]. Recently, Puskas and Luo[38] reported that initiation of styrene by 2-chloro-2,4,4-trimethylpentane (TMPCl) in conjunction with $TiCl_4$ at −75 °C in MeCHx/MeCl 60/40 (v/v) is first order in [$TiCl_4$] at [TMPCl] > [$TiCl_4$]. Our results and that of Storey et al.,[39] however, contradict this finding.

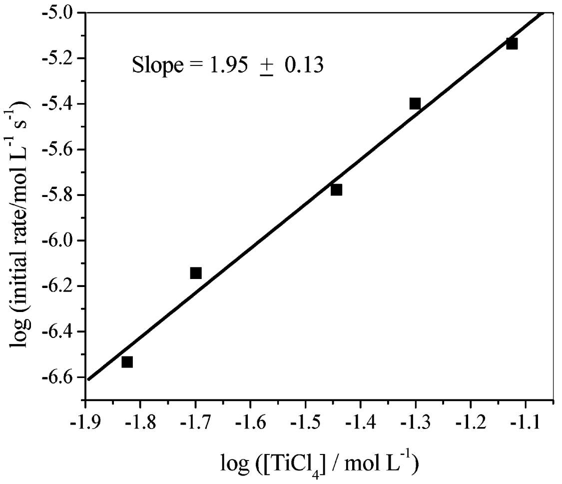


Figure 5. Bilogarithmic plot of the initial rate of capping vs the concentration of $TiCl_4$ for determining the order with respect to $TiCl_4$ in the capping reaction of **1-Cl** (0.002 mol L^{-1}) with [DTE] = 0.002 mol L^{-1} and [DTBP] = 0.004 mol L^{-1} in MeCHx/MeCl 60/40 (v/v) at −80 °C.

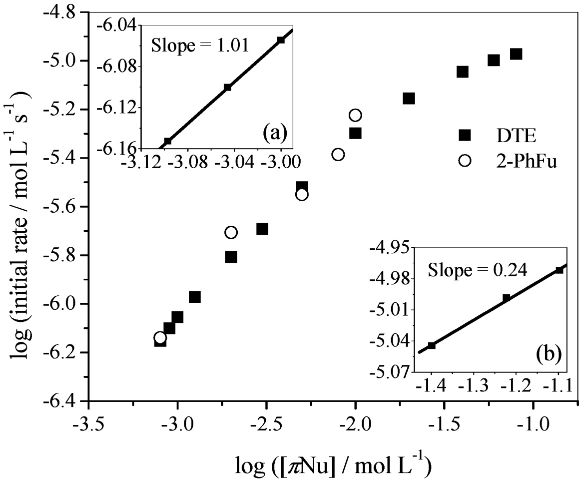


Figure 6. The log(initial rate of capping) vs log [DTE] for the capping reaction of **1-Cl** with DTE and 2-PhFu in MeCHx/MeCl 60/40 (v/v) at −80 °C; [**1-Cl**] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1}. Inset: plot of log (initial rate of capping) vs log [DTE] at (a) [DTE] = 0.0008−0.001 mol L^{-1} and (b) [DTE] = 0.04−0.08 mol L^{-1}.

According to eq 7a, the capping reaction should be first order with respect to [πNu] when $k_{-i} \gg k_c[\pi Nu]$, which has been observed for the capping reaction of **1-Cl** with DTE at [DTE] ≤ 0.001 mol L^{-1}. According to eq 7b, the capping rate should be independent of [DTE] when $k_{-i} \ll k_c[DTE]$, e.g., at high DTE concentrations. The log(initial rate of capping) vs log [πNu] plots for the capping reaction of **1-Cl** with DTE and 2-PhFu are shown in Figure 6. In Figure 6, insets a and b show the corresponding bilogarithmic plots of the initial capping rates as a function of [DTE], which indeed confirm first-order dependence on [DTE] in the DTE concentration range 0.001−0.0008 mol L^{-1} and 0.24 order dependence on [DTE] in the concentration range 0.04−0.08 mol L^{-1}, respectively. The DTE concentration could not be increased above 0.08 mol L^{-1} because above that concentration DTE precipitates out from the reaction medium.

For the accurate determination of the apparent rate constant of capping, $k_cK_i^{app}$, and the apparent rate constant of ionization, k_i^{app} ($k_i^{app} = k_iK_{D0}$, where k_i is the absolute rate constant of ionization and K_{D0} is the equilibrium constant of $TiCl_4$ dimerization), the reciprocal initial rate of capping was plotted as a function of 1/[πNu].

$$\frac{[\mathbf{1\text{-}Cl}][\mathrm{TiCl_4}]^2}{\frac{d}{dt}([\mathbf{1}\text{-}\pi\mathrm{Nu}^+\mathrm{Ti_2Cl_9}^-] + [\mathbf{1}\text{-}\pi\mathrm{Nu}^+])} = \frac{1}{k_cK_i^{app}[\pi\mathrm{Nu}]} + \frac{1}{k_i^{app}} \quad (8)$$

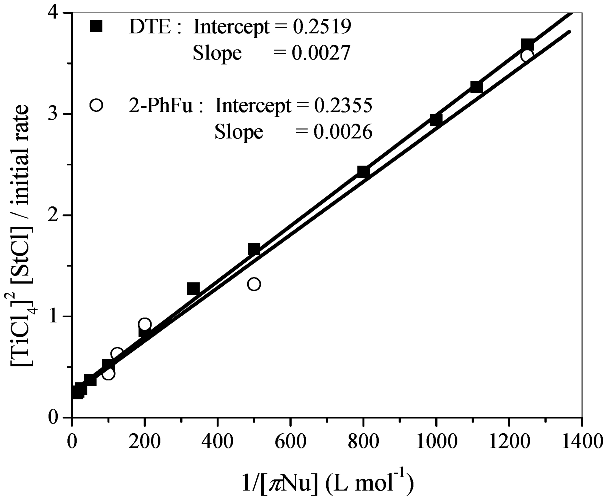


Figure 7. Plot of reciprocal initial rate of capping vs 1/[πNu] for the capping reaction of **1-Cl** with DTE and 2-PhFu in MeCHx/MeCl 60/40 (v/v) at −80 °C; [**1-Cl**] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1}.

According to eq 8, which is the reciprocal of eq 6, the reciprocal initial rate of capping vs 1/[πNu] plot should yield a straight line, with the slope and intercept of $1/k_cK_i^{app}$ and $1/k_i^{app}$, respectively (Figure 7). In Figure 7, from the intercept $k_i^{app} = 3.97$ L^2 mol^{-2} s^{-1} and from the slope $k_cK_i^{app} = 365$ L^3 mol^{-3} s^{-1} were calculated. With $E = 9.6$ determined for $\mathbf{1}^+$ above, the LFER suggest diffusion-limited addition of 2-PhFu ($N = 3.6$)[40] to $\mathbf{1}^+$. Although the N parameter for DTE is unknown, the identical plots in Figures 6 and 7 obtained with both DTE and 2-PhFu suggest diffusion-limited addition with both nucleophiles. Therefore, from $k_cK_i^{app}$ and the known value of diffusion-controlled second-order rate constant $k_c = 3 \times 10^9$ L mol^{-1} s^{-1}, $K_i^{app} = 12.2 \times 10^{-8}$ L^2 mol^{-2} at −80 °C was calculated. This K_i^{app} value is about 2.5 times higher than that reported earlier, obtained in the addition reaction of DTE to dimeric styryl living ends in 70/30 $CHCl_3/CH_2Cl_2$ (v/v) at −75 °C using on-line visible spectroscopy.[9] This difference may be due to the different solvent system and temperature. Using eq 2, $k_{-i} = 3.25 \times 10^7$ s^{-1} was obtained.

Considering that the ionization constant of the dormant polystyrene chain ends is similar to that of **1-Cl**, K_i^{app} allows us to calculate the concentration of active chain ends. From the apparent rate constant of propagation for St (see in the next section) and the concentration of active chain ends, $k_p^{\pm} = 1.6 \times 10^9$ L mol^{-1} s^{-1} was calculated. This value agrees well with that estimated from the LFER (eq 1) but is much higher than that previously accepted.

Competition Experiments. Competition experiments, i.e., polymerizations carried out in the presence of a capping πNu (DTE or 2-PhFu), were also used to determine the propagation rate constant in the carbocationic polymerization of St (Scheme 7). The polymerization stops when all chain ends are capped by the πNu, since the capped chain ends are too stable to initiate polymerization. Both conversion and number-average degrees of polymerization reach a limiting value. From the limiting conversion (x_∞^{St}) and number-average degree of polymerization ($DP_{n,\infty}$), the reactivity ratio $k_p^{\pm}/k_c^{\pm}$ can be calculated using eqs 9 and 10.[11,41]

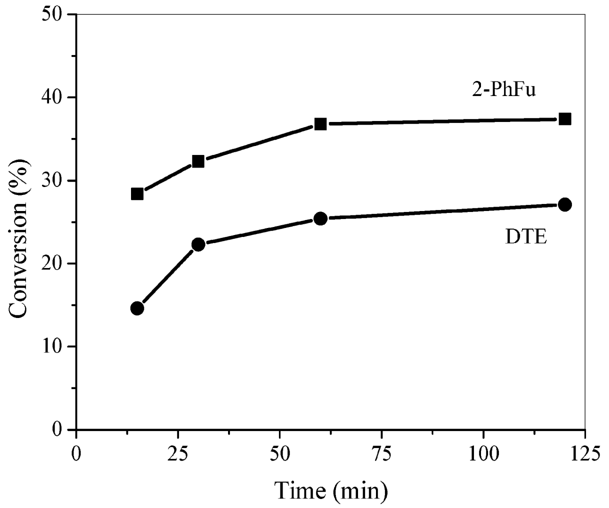


Figure 8. Time vs conversion plot in the competition experiment with St; [p-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [St] = 0.2 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1}, [2-PhFu] = 0.003 mol L^{-1}, and [DTE] = 0.009 mol L^{-1} in MeCHx/MeCl 60/40 (v/v) at −80 °C.

$$\frac{k_p^{\pm}}{k_c^{\pm}} = \frac{\ln(1 - x_\infty^{St})}{\ln(1 - [p\text{-MeStCl}]_0/[\pi\text{Nu}]_0)} \tag{9}$$

$$\frac{k_p^{\pm}}{k_c^{\pm}} = \frac{\ln(1 - DP_{n,\infty}[p\text{-MeStCl}]_0/[\text{St}]_0)}{\ln(1 - [p\text{-MeStCl}]_0/[\pi\text{Nu}]_0)} \tag{10}$$

In eqs 9 and 10, [πNu]$_0$ is the initial πNu concentration, [p-MeStCl]$_0$ is the initiator concentration, which equals that of the chain ends, and [St]$_0$ is the initial concentration of St. The cationic polymerization of St was carried out in the presence of either DTE (= 0.009 mol L^{-1}) or 2-PhFu (= 0.003 mol L^{-1}) with $TiCl_4$ as co-initiators at −80 °C in MeCHx/MeCl 60/40 (v/v) solvent system in the presence of proton trap, DTBP. Limiting conversion (for 2-PhFu $x_\infty^{St} = 36.8\%$, $M_{n,GPC} = 3920$, PDI = 1.8; for DTE, $x_\infty^{St} = 25.4\%$, $M_{n,GPC} = 2800$, PDI = 1.8) was reached in less than 100 min with both πNu (Figure 8). The time to reach the x_∞^{St} was independent of the πNu used.

Scheme 7. Competition Experiment with πNu

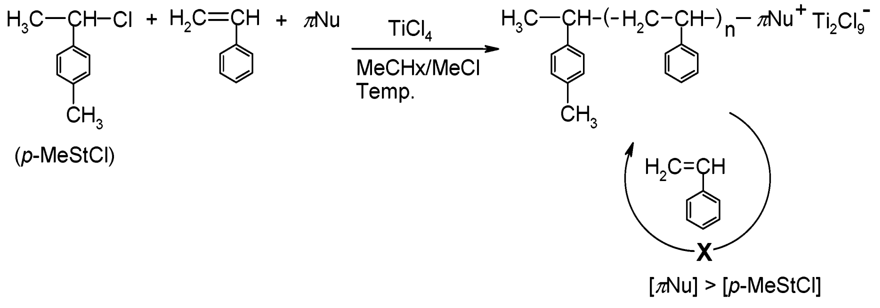


Table 1. Initial Slope and the Apparent Rate Constants of Capping, $k_cK_i^{app}$, for the Capping Reaction of 1-Cl with DTE in MeCHx/MeCl 60/40 (v/v)[a]

temp (°C)	$k_{app}{}^b$ (s^{-1})	initial slope (s^{-1})	$k_cK_i^{app}$ ($L^3\ mol^{-3}\ s^{-1}$)	k_c ($L\ mol^{-1}\ s^{-1}$)	$K_i^{app} \times 10^8$ ($L^2\ mol^{-2}$)	$k_p^{\pm}$ ($L\ mol^{-1}\ s^{-1}$)
−80	5.2×10^{-4}		365.0	3.0×10^9	12.2	1.6×10^9
−70	3.3×10^{-4}	5.82×10^{-4}	255.2	3.7×10^9	6.9	1.8×10^9
−60	2.4×10^{-4}	5.03×10^{-4}	220.5	4.3×10^9	5.1	1.8×10^9
−50	1.6×10^{-4}	4.22×10^{-4}	185.0	5.0×10^9	3.7	1.7×10^9

[a] [**1-Cl**] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1}, and [DTE] = 0.001 mol L^{-1}. [b] From the first-order plot of ln ($[M]_0/[M]$) vs time for the cationic polymerization of St using [St] = 0.5 mol L^{-1}, [*p*-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1}.

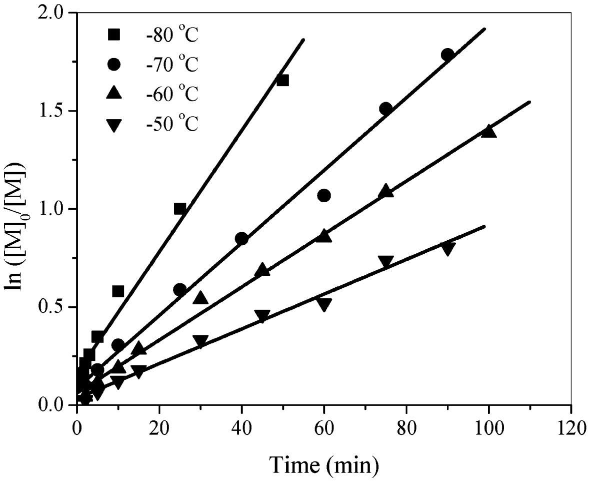


Figure 9. First-order plot of ln ($[M]_0/[M]$) vs time for the cationic polymerization of St initiated by *p*-MeStCl/$TiCl_4$; [*p*-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [St] = 0.5 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1} in MeCHx/MeCl 60/40 (v/v) at −80 °C.

The M_n of the polymer calculated by ^1H NMR spectroscopy assuming one πNu moiety per chain was in good agreement with that determined by GPC, suggesting complete capping of the polystyryl cation (PSt^+) and the absence of side reactions such as proton elimination and inter- or intramolecular alkylation. The molecular weight distributions (M_w/M_n) of the polymers obtained in the competition experiment were close to the expected most probable distribution ($M_w/M_n \approx 2$). The $k_p^{\pm}/k_c^{\pm}$ values were calculated from x_{∞}^{St} using eq 9 and from $DP_{n,\infty}$ using eq 10. From the average values of $k_p^{\pm}/k_c^{\pm}$ for 2-PhFu and DTE, $k_p^{\pm} = 1.3 \times 10^9$ and 3.6×10^9 L mol^{-1} s^{-1} were calculated, respectively, by assuming $k_c^{\pm} = 3 \times 10^9$ L mol^{-1} s^{-1}. The difference between $k_p^{\pm}$ determined with 2-PhFu and DTE is most likely due to the somewhat different diffusion coefficients, as reported already.[41] The $k_p^{\pm}$ values are in good agreement with those obtained from the on-line UV−vis spectroscopy and with that predicted by the linear free energy relationship, however, 6 orders of magnitude higher than that previously reported by the stopped-flow method. Since determination of the rate of monomer consumption in the earlier experiments[6−8] cannot be that erroneous, the most plausible explanation for this huge difference is that the assumption that all UV−vis absorbing species participate in propagation is incorrect. The need to identify what fraction of the absorbance is due to propagating species has already been emphasized by Plesch in a critical reexamination of spectroscopic determination of growing ends for the determination of propagation rate constants.[3]

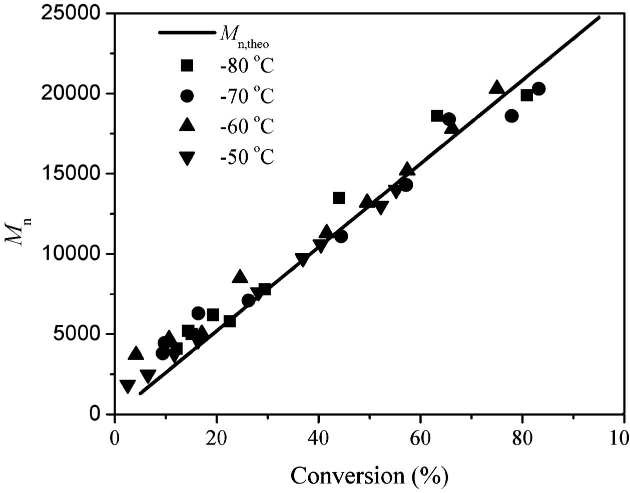


Figure 10. Variation of M_n with conversion. Reaction conditions are the same as in Figure 9.

Table 2. Limiting Conversion, Molecular Weight, and Absolute Propagation Rate Constants in the Competition Reactions of St Polymerization in MeCHx/MeCl 60/40 (v/v) at Different Temperatures[a]

temp (°C)	conv (%)	M_n (GPC)	PDI	$k_p^{\pm}/k_c^{\pm}$ (x_{∞}^{St})	$k_p^{\pm}/k_c^{\pm}$ ($DP_{n,\infty}$)	$k_p^{\pm} \times 10^{-9}$ ($L\ mol^{-1}\ s^{-1}$)
−80	36.8	3920	1.8	0.42	0.44	1.3
−70	34.4	3750	1.8	0.38	0.41	1.5
−60	33.1	3680	2.1	0.37	0.40	1.7
−50	32.3	3280	1.9	0.35	0.34	1.7

[a] [*p*-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [St] = 0.2 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1}, and [2-PhFu] = 0.003 mol L^{-1}.

Effect of Temperature on the Rate Constants. First, the cationic polymerization of styrene was carried out in MeCHx/MeCl 60/40 (v/v) using the *p*-MeStCl/$TiCl_4$ initiating system in the presence of DTBP as a proton trap at −80, −70, −60, and −50 °C ([St] = 0.5 mol L^{-1}, [*p*-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1}). The ln ($[M]_0/[M]$) vs time and M_n vs percent conversion plots are shown in Figures 9 and 10, respectively. For polymerizations at all temperatures the PDI decreased with increasing conversion. The apparent rate constants of propagation (k_{app}) were obtained from the first-order plot of ln ($[M]_0/[M]$) vs time and presented in Table 1. Polymerizations were also carried out in the absence of initiator, *p*-MeStCl (direct initiation). Under the same conditions, 3.5%, 7.8%, and 12.1% monomer conversions were obtained after 1, 2, and 3 h, respectively. This confirms that direct initiation is operational but very slow compared to initiation with the initiator, *p*-MeStCl. Interestingly, all first-order plots exhibit a positive intercept, which decreases with increasing temperature. This phenomenon has been first reported by Storey et al.[42,43] and explained by the different ionization rate constant of the initiator and the dormant polymer end (see later).

Table 3. k_i^{app}, k_{-i}, and K_i^{app} Values from RMC and the Conversion−Polydispersity Curves in MeCHx/MeCl 60/40 (v/v)[a]

T (°C)	β	k_i^{app} (from β and K_i^{app}) (L^2 mol^{-2} s^{-1})	k_i^{app} (from RMC) (L^2 mol^{-2} s^{-1})	k_{-i} (from β) (s^{-1})	k_{-i} (from RMC and K_i^{app}) (s^{-1})
−80	9.6	3.9	2.67	4.7×10^7	2.2×10^7
−70	16.5	4.2	3.03	8.1×10^7	4.4×10^7
−60	25.8		3.11		6.1×10^7
−50	41.4		3.62		10.2×10^7

[a] [*p*-MeStCl] = 0.002 mol L^{-1}, [St] = 0.5 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1}.

Visible spectroscopic studies of the capping reaction of **1-Cl** with DTE were also carried out at −70, −60, and −50 °C. In the previous section we have already shown that at −80 °C at [DTE] ≤ 0.001 mol L^{-1} $k_{-i} \gg k_c[\pi Nu]$, and the simplified eq 7a can be used to determine $k_cK_i^{app}$. Since $k_{-i} \gg k_c[\pi Nu]$ must also be valid at higher temperature (k_{-i} increases with temperature while k_c is hardly affected), all capping reactions were carried out at [DTE] = 0.001 mol L^{-1}. The $k_cK_i^{app}$ values calculated from the initial slopes of the absorption vs time plots are presented in Table 1. The K_i^{app} values vary little in the temperature range of −80 to −50 °C. From the apparent rate constant of propagation for St and the concentration of active chain ends, the absolute rate constant of propagation for ion pairs, $k_p^{\pm}$, was calculated using the diffusion-limited second-order rate constant $k_c^{\pm} = 3 \times 10^9$ L mol^{-1} s^{-1} in MeCHx/MeCl 60/40 (v/v) solvent system at −80 °C. Although diffusion-limited reactions do not have an enthalpic barrier, their observed activation energy will not be zero but will be determined by the temperature dependence of the diffusion coefficients, which is related to the viscosity (η) of the solution. The k_c values at other temperatures have been obtained (Table 1) by applying the Stokes−Einstein equation $D = RT/6\pi\eta rN$, where D is the diffusion coefficient, R is the universal gas constant, η is the dynamic viscosity of the system, r is the radius of the molecule, and N is Avogadro's number. Since the activation energy for the flow to occur is usually very small (≈2 kcal mol^{-1}),[41] we have used the viscosity data of hexanes/MeCl solvent mixtures of different solvent polarity and temperature determined earlier to calculate the k_c values in MeCHx/MeCl solvent mixtures at the corresponding temperature. The $k_p^{\pm}$ values at different temperatures are tabulated in Table 1. In agreement with the conclusion of Mayr that fast bimolecular reactions do not have an enthalpic barrier,[32,33] the $k_p^{\pm}$ values are virtually independent of temperature. A slight increase in $k_p^{\pm}$ with the increase of temperature is expected as the viscosity of the solution also affects $k_p^{\pm}$.

In addition to the capping studies of **1-Cl**, competition experiments were also carried out at different temperatures using 2-PhFu as capping agent. Table 2 shows the results of competition experiments. The molecular weight calculated by ^{1}H NMR spectroscopy from the ratio of the intensities of phenyl proton signals in the aromatic region in polystyrene to the signal at 5.9 ppm from 2-PhFu moiety at the chain end and that measured by GPC are similar, indicating that the chain ends are completely capped with the πNu. This is important especially for the experiments carried out at −60 or −50 °C where indanic cyclization may be operational during the competition experiments. The results indicate that indanic cyclization is much slower than capping. The polydispersity index of the polymers obtained after the competition experiment was close to the expected most probable distribution (≈2).

The $k_p^{\pm}/k_c^{\pm}$ values were calculated from x_{∞}^{St} using eq 9 and from $DP_{n,\infty}$ using eq 10. Using the $k_c^{\pm}$ values at different temperatures, the two methods yielded similar $k_p^{\pm}$ values, which were virtually independent of temperature (Table 2). (Similarly to $k_c^{\pm}$, since $k_p^{\pm}$ is nearly diffusion limited, it is also slightly affected by change in solution viscosity with changing temperature.) The $k_p^{\pm}$ values are in excellent agreement with those determined by UV−vis study of the capping reaction of **1-Cl**.

Determination of k_i^{app}, k_{-i}, and K_i^{app}. Storey et al. recently[42] reported that the average number of monomer units added per ionization−termination cycle, called the run number[44] (RN = $k_p^{\pm}[M]/k_{-i}$), can be determined by analysis of an initiation event they coined rapid monomer consumption (RMC). From RN and the apparent rate constant of propagation (k_{app}), k_i^{app} can be calculated by using the following equation:

$$k_{app} = k_p^{\pm}\frac{k_i^{app}}{k_{-i}}[I][TiCl_4]^2 = k_i^{app}\frac{RN}{[M]}[I][TiCl_4]^2 \quad (11)$$

where [I] is the initiator concentration and $k_p^{\pm}/k_{-i}$ = RN/[M]. When K_i or $k_p^{\pm}$ is known, k_{-i} can also be obtained. From the k_{app} (obtained from the first-order plot of ln ([M]$_0$/[M]) vs time) and using [I] = 0.002 mol L^{-1}, [M] = 0.5 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1}, the values of k_i^{app} were determined at different temperatures and presented in Table 3. The k_i^{app} value of 2.67 L^2 mol^{-2} s^{-1} obtained at −80 °C is in reasonable agreement with that of 3.97 L^2 mol^{-2} s^{-1} obtained from UV−vis measurement of capping of **1-Cl**. Using K_i^{app} (Table 1), k_{-i} values were also calculated at different temperatures and tabulated in Table 3.

The k_{-i} value at different temperatures in MeCHx/MeCl 60/40 (v/v) was also determined from the polydispersity vs conversion plot, by curve fitting to eq 12 described by Müller et al.[45]

$$\bar{M}_w/\bar{M}_n = 1 + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \quad (12)$$

where x is conversion, $\bar{M}_w/\bar{M}_n$ is polydispersity index, and β value is related to k_{-i}, $k_p^{\pm}$, and the initiator concentration $[I]_0$ by $k_{-i} = [I]_0k_p^{\pm}\beta$. By knowing K_i^{app} (from k_{app} and $k_p^{\pm}$) and k_{-i}, k_i^{app} was also calculated. The polydispersity vs conversion plot obtained with the *p*-MeStCl/$TiCl_4$ initiating system for MeCHx/MeCl 60/40 (v/v) at −80 °C is shown in Figure 11. At −60 and −50 °C fitting of the polydispersity vs conversion curve was rather poor, most likely due to termination,[46] and therefore we were not able to calculate k_{-i} and k_i^{app}. The results are shown in Table 3. There is an excellent agreement between k_i^{app} obtained at −80 °C from the

Table 4. k_{app}**, Limiting Conversion, Limiting** M_n**, and** $k_p^{\pm}$ **in Different Solvent Mixtures**[a]

(MeCHx + St)/ MeCl (v/v)	$k_{app}{}^{b}$ (s^{-1})	conv (%)	M_n (GPC)	PDI	$k_p^{\pm}/k_c^{\pm}$ (x_{∞}^{St})	$k_c^{\pm}$ (L mol^{-1} s^{-1})	$k_p^{\pm} \times 10^{-9}$ (L mol^{-1} s^{-1})
80/20	1.9×10^{-4}	21.1	2340	1.9	0.94	2.2×10^{9}	2.07
60/40	5.2×10^{-4}	25.4	2800	1.8	1.17	3.0×10^{9}	3.5
50/50	1.2×10^{-3}	34.0	3590	2.0	1.65	3.5×10^{9}	5.8
40/60	3.4×10^{-3}	39.1	3910	1.8	1.97	3.9×10^{9}	7.7

[a] [*p*-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [St] = 0.2 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1}, and [DTE] = 0.009 mol L^{-1} at −80 °C. [b] From the first-order plot of ln ($[M]_0$/[M]) vs time for the cationic polymerization of St using [St] 0.5 mol L^{-1}, [*p*-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1} at −80 °C.

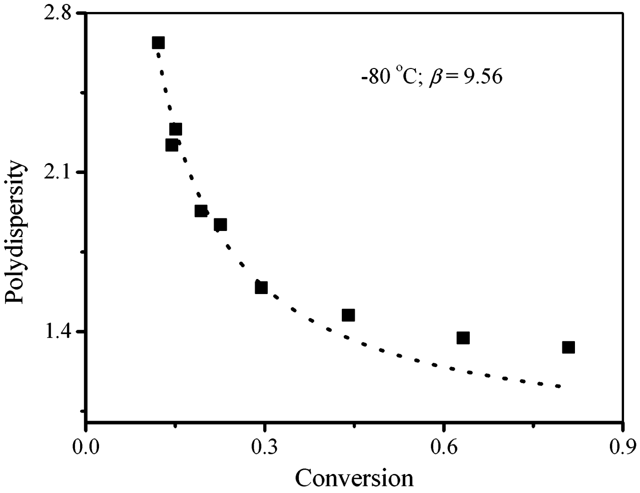


Figure 11. Polydispersity vs conversion curve for the polymerization of styrene in MeCHx/MeCl 60/40 (v/v) at −80 °C; [St] = 0.5 mol L^{-1}, [*p*-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1}.

polydispersity vs conversion plot and that determined by capping studies. The K_i^{app} value determined in this study is somewhat higher than the $K_i^{app} = 1.3$ L^2 mol^{-2} s^{-1} reported recently, determined by the rapid monomer consumption method in the cationic polymerization of St initiated with 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene/$TiCl_4$ in MeCHx/ MeCl 60/40 (v/v) at −70 °C.[43]

The cationic polymerization of St at −80 °C in MeCHx/MeCl 60/40 (v/v) results a β value of 9.6. This value corresponds to $k_p^{\pm}/k_{-i} = 49$; i.e., propagation is 49 times faster than reversible termination. This value is in excellent agreement with that determined by visible spectroscopy where $k_p^{\pm}/k_{-i} = 52$ was calculated. In Table 3, the β value increases with the increase of temperature, suggesting that the rate constant of deactivation increases with increasing temperature, since $k_p^{\pm}$ remains constant over the temperature range studied here. Therefore, while on average 49 monomer units are added during an active cycle at −80 °C, only 30 (equivalent RN = 39 in ref 41) monomer units are incorporated during an active cycle at −70 °C. For the cationic polymerization of St there is a small decrease of k_{app} with increasing temperature, while in the living carbocationic polymerization of isobutylene this decrease was rather large.[41] This is due to a much smaller decrease of K_i^{app} for St with increasing temperature.

The apparent activation energy of polymerization, $E_a = -3.3$ kcal mol^{-1}, was calculated from the Arrhenius plot of ln (k_{app}) vs 1/*T*. Storey and Thomas[43] reported an E_a of −3.8 kcal mol^{-1} for the polymerization of St initiated with 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene/$TiCl_4$ in MeCHx/MeCl 60/40 (v/v) solvent mixture. Both visible spectroscopic studies and competition experiments show that the absolute rate constant of propagation is independent of temperature. However, the apparent rate constant of propagation is affected by the temperature-dependent ionization equilibrium. For St, K_i^{app} is very small (Table 1); the chain ends are predominantly in the dormant state. Decreasing the reaction temperature shifts this equilibrium toward the active state. Thus, the negative E_a can be attributed to the decreasing active center concentration with increasing temperature.

From the slope of the Eyring plot of ln(k_{app}/*T*) vs 1/*T*, the standard enthalpy of activation, $\Delta H^{\circ\ddagger} = -3.7$ kcal mol^{-1} was calculated. Since the propagation of St does not have an enthalpic barrier, $\Delta H^{\circ\ddagger}$ must include the sum of the enthalpy of ionization and titanium halide dimerization.

The apparent values of $\Delta H^{\circ} = (\Delta H_i^{\circ} + \Delta H_{D0}^{\circ}) = -3.3$ kcal mol^{-1} and $\Delta S^{\circ} = (\Delta S_i^{\circ} + \Delta S_{D0}^{\circ}) = -49$ cal mol^{-1} K^{-1} for the ionization process have been obtained from the temperature dependence of K_i^{app}. These values show that the ionization process is exothermic and exoentropic.

Effect of Solvent Polarity on the Rate Constants. In a series of experiments the cationic polymerization of St was carried out in MeCHx/MeCl solvent mixture of varying composition from 80/20 to 40/60 (v/v) at −80 °C. The first-order plots of ln ($[M]_0$/[M]) vs time were linear, indicating absence of termination during the polymerization up to ∼80% monomer conversions. The molecular weights follow the theoretical M_n−conversion line, indicating the absence of chain transfer during the polymerization in all solvent mixtures. The first-order apparent rate constants of propagation were obtained from the first-order plot of ln ($[M]_0$/[M]) vs time. The k_{app} value, shown in Table 4, increases with increasing polarity of the reaction medium.

Competition experiments were also carried out in different MeCHx/MeCl solvent mixtures to understand the effect of solvent polarity on the absolute rate constant of propagation. Direct initiation is operational in the competition experiments with DTE, and therefore, competition experiments in the absence of initiator with DTE were also carried out, and the conversion values were subtracted. The $k_p^{\pm}/k_c^{\pm}$ values were calculated from eq 9. To determine $k_p^{\pm}$, the value of $k_c^{\pm}$ at different solvent polarity was estimated using the viscosity data of hexanes/MeCl solvent mixture of different solvent polarity.[41] The $k_p^{\pm}$ value increases slightly with increasing solvent polarity (Table 4). This is similar to our results with isobutylene[41] and also similar to the solvent effect reported for the reaction of 2-methyl-1-pentene with the bis(*p*-methoxyphenyl)carbenium ion in different solvents.[47] Since we have shown above that propagation of St does not have an enthalpic barrier, solvent polarity may only affect the entropy of activation. It is unclear at present, however, how increasing solvent polarity decreases the entropic barrier.

Table 5. k_{app}, Limiting Conversion, Limiting M_n, and $k_p^{\pm}$ Value in CH_2Cl_2 at −15 °C[a]

conv (%)	k_{app} (s^{-1})	M_n (GPC)	PDI	$M_{n,theo}$	$k_p^{\pm}/k_c^{\pm}$ (x_{∞}^{St})	$k_p^{\pm}/k_c^{\pm}$ ($DP_{n,\infty}$)	$k_p^{\pm} \times 10^{-9}$ (L mol^{-1} s^{-1})
28.4	2.6×10^{-4}	1570	1.8	1480	1.92	2.06	8.4

[a] [**1-Cl**] = 0.02 mol L^{-1}, [$SnCl_4$] = 0.1 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [St] = 1.0 mol L^{-1}, and [2-PhFu] = 0.125 mol L^{-1}.

Effect of Lewis Acid. The living cationic polymerization of St is also reported in the literature using the **1-Cl**/$SnCl_4$ initiating system at −15 °C in CH_2Cl_2 solvent.[48] Therefore, we chose $SnCl_4$ to understand the effect of the nature of Lewis acid on $k_p^{\pm}$. Competition experiments with DTE or 2-PhFu were carried out with the **1-Cl**/$SnCl_4$ initiating system in CH_2Cl_2 at −15 °C. In the case of DTE, the color of the solution changed from deep red to red and finally to green in 1 h. This indicates that the PSt-DTE$^+$ cation is not stable in CH_2Cl_2 at −15 °C, and 100% conversion was reached even at very high πNu concentration (0.125 mol L^{-1}). Therefore, experimentation with DTE was discontinued. With 2-PhFu, however, limiting conversion was reached in 6 h. Since $SnCl_4$ is a weak Lewis acid, the time needed to reach the limiting conversion is much higher than with $TiCl_4$. The results of the competition experiment with 2-PhFu are presented in Table 5. The molecular weight determined by GPC is in good agreement with the theoretical molecular weight. The molecular weight calculated by ^1H NMR spectroscopy (from the ratio of the integral intensities of the phenyl proton signals in the aromatic region in polystyrene to the signal at 5.9 ppm from 2-PhFu moiety at the chain end) is similar to the M_n measured by GPC, which indicates that the chain ends are completely capped with the πNu. The calculated $k_p^{\pm}/k_c^{\pm}$ reactivity ratios based on x_{∞}^{St} and $DP_{n,\infty}$ are also shown in Table 5. Using 0.64 cP[49] for the viscosity of CH_2Cl_2 at −15 °C, $k_c^{\pm} = 4.2 \times 10^9$ L mol^{-1} s^{-1} is obtained, from which $k_p^{\pm} = 8.4 \times 10^9$ L mol^{-1} s^{-1} is calculated in CH_2Cl_2 at −15 °C. This value is similar to the $k_p^{\pm}$ values obtained at −80 °C using $TiCl_4$ as Lewis acid in the most polar solvent mixture used. Although the apparent rate constants of propagation are very different for $TiCl_4$ and $SnCl_4$, the $k_p^{\pm}$ value is similar for both Lewis acids. That the nature of Lewis acid does not affect the $k_p^{\pm}$ is in line with that we reported recently for the polymerization of isobutylene.[41]

Conclusion

Cationic propagation of styrene is essentially diffusion-limited according to predictions by the linear free energy relationship and experimental determination of $k_p^{\pm} = 2 \times 10^9$ L mol^{-1} s^{-1} in conjunction with $TiCl_4$ in methylcyclohexane/methyl chloride 60/40 (v/v) at −80 °C. Previously accepted values, which are 6 orders of magnitude lower, seriously underestimate the propagation rate constant. In agreement with Mayr's finding that fast reactions of carbocations with π-systems do not show temperature dependence,[32] $k_p^{\pm}$ is independent of temperature, and thus cationic propagation of styrene proceeds with an activation energy of zero. The propagation rate constant is independent of the nature of Lewis acid, which seems to be a general observation as already reported for isobutylene. The observed small change in overall polymerization rates at different temperature, which is characterized by a small $E_a = -3.3$ kcal mol^{-1}, is due to a small variation in k_i^{app} and k_{-i} with temperature.

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Supporting Information Available: Relative reactivities of (2-methylallyl)trimethylsilane (**2a**) and allyltrimethylsilane (**2b**) toward the cation **1**$^+$ (CH_2Cl_2, −78 °C), Table 1; relative reactivities of (2-methylallyl)trimethylsilane (**2a**) and triphenylsilane (**2c**) toward the cation **1**$^+$ (CH_2Cl_2, −78 °C), Table 2; relative reactivities of (2-methylallyl)trimethylsilane (**2a**) and dimethylphenylsilane (**2d**) toward the cation **1**$^+$ (CH_2Cl_2, −78 °C), Table 3; relative reactivities of (2-methylallyl)trimethylsilane (**2a**) and allyltrimethylsilane (**2b**) toward the cation **4**$^+$ (CH_2Cl_2, −78 °C), Table 4; relative reactivities of (2-methylallyl)trimethylsilane (**2a**) and triphenylsilane (**2c**) toward the cation **4**$^+$ (CH_2Cl_2, −78 °C), Table 5; Arrhenius plot of ln(k_{app}) vs 1/T to determine apparent activation energy of polymerization, Figure 1; plot of ln(k_{app}/T) vs 1/T to determine the standard enthalpy of activation, $\Delta H^{\circ\ddagger}$, Figure 2. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Part of this work was presented at the 225th ACS National Meeting in New Orleans [De, P.; Munavalli, M. V.; Faust, R. *Polym. Prepr.* **2003**, *44* (1), 1071−1072] and the 226th ACS National Meeting in New York [De, P.; Munavalli, M. V.; Faust, R. *Polym. Prepr.* **2003**, *44* (2), 920−921].

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