Determination of the Absolute Rate Constants of Propagation for Ion Pairs in the Carbocationic Polymerization of *p*-Chlorostyrene

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Introduction

The determination of rate constants in the living carbocationic polymerization of isobutylene (IB), styrene (St), and styrene derivatives has been the focus of our recent activities. We recently reported on the absolute rate constants of propagation for ion pairs ($k_p^{\pm}$) in the cationic polymerization of IB,[1,2] St,[3] *p*-methoxystyrene (*p*-MeOSt),[4] and 2,4,6-trimethylstyrene (TMeSt)[5] determined by two diffusion clock methods: competition experiments and kinetic studies of diffusion-limited addition of π-nucleophiles by on-line UV−vis spectroscopy. For all these monomers, the $k_p^{\pm}$ values obtained from the competition experiments agreed well with those determined from on-line UV−vis spectroscopic measurements. For the cationic polymerization of *p*-chlorostyrene (*p*-ClSt) in ethylene dichloride $k_p = 290$ L mol^{-1} min^{-1} at 25 °C in the perchloric acid-mediated polymerization[6] and 300 L mol^{-1} min^{-1} at 30 °C in the H_2SO_4-mediated polymerization[7] have been reported. In light that in agreement with the prediction by Mayr's linear free energy relationship[3,8] the recently developed diffusion clock methods demonstrated diffusion-limited propagation for styrene,[3] it was of interest to study k_p for the living cationic polymerization of *p*-ClSt.

Living cationic polymerization of *p*-ClSt was studied by a number of groups using a variety of initiating systems and solvents. Kennedy et al.[9] reported the living carbocationic polymerization of *p*-ClSt initiated by 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ in the presence of dimethylacetamide as electron donor and 2,6-di-*tert*-butylpyridine (DTBP) as proton trap in methyl chloride (MeCl)/methylcyclohexane (MeCHx) 60/40 (v/v) solvent mixture at −80 °C. Kanaoka et al. obtained poly(*p*-ClSt) of a narrow molecular weight distribution with 1-phenylethyl chloride (StCl)/$SnCl_4$ initiating system in CH_2Cl_2 at −15 to +25 °C in the presence of nBu$_4$NCl.[10] The rate of polymerization was somewhat slow. Controlled cationic polymerization of *p*-ClSt was also achieved by the alcohol/BF_3OEt_2 system in the presence of a fairly large amount of water.[11] Recently, for the living polymerization of styrene (St) the 1-chloro-1-(4-methylphenyl)ethane (*p*-MeStCl)/$TiCl_4$ initiating system was found to be more efficient than TMPCl/$TiCl_4$ in the MeCl/MeCHx 40/60 (v/v) solvent mixture at −80 °C.[12] In this note, two different initiators *p*-MeStCl and 1-chloro-1-(*p*-chlorophenyl)ethane (*p*-ClStCl), a model propagating end, in conjunction with $TiCl_4$ and DTBP were used to study the living cationic polymerization of *p*-ClSt in MeCHx/MeCl 60/40 (v/v) solvent mixture at −80 °C. The $k_p^{\pm}$ value has been determined by competition experiments and UV−vis monitoring of the capping reaction of *p*-ClSt cation with 1,1-di-*p*-tolylethylene (DTE) or 2-phenylfuran (2-PhFu).

Experimental Section

Materials. *p*-Chlorostyrene (*p*-ClSt, Aldrich, 97%) 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 CaH_2 under reduced pressure. The *p*-ClStCl was synthesized by hydrochlorination of *p*-ClSt in CH_2Cl_2 1:10 (v/v) at 0 °C.[3] After removing CH_2Cl_2 on the rotary evaporator it was purified by vacuum distillation from CaH_2. ^{1}H NMR spectrum: 7.41 (s), 5.12 (q), and 1.90 ppm (d). Other chemicals such as 1,1-di-*p*-tolylethylene (DTE) or 2-phenylfuran (2-PhFu) and solvents were purified as described previously or used as received.[3]

Polymerization. Polymerizations were carried out in culture tubes under a dry nitrogen atmosphere in an MBraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA), as described elsewhere.[3]

Characterization. Molecular weights were measured using a Waters HPLC system equipped with a model 510 HPLC pump, a model 250 dual refractometer/viscometer detector (Viscotek), a model 486 UV/vis detector, a model 712 sample processor, and five ultra-Styragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL/min at room temperature. The number-average molecular weights (M_n) and polydispersities (PDI) were determined using the conventional calibration curve and Viscotek TriSEC GPC software. ^{1}H NMR spectroscopy was carried out on a Bruker 250 MHz spectrometer using $CDCl_3$ as a solvent. UV−vis spectroscopic measurements were carried out under a dry nitrogen atmosphere in the glovebox, as described elsewhere.[3]

Reaction Procedures for UV−Vis Spectroscopic Experiments. A solution of *p*-ClStCl, DTBP, and $TiCl_4$ in MeCHx/MeCl 60/40 (v/v) solvent was kept in the glovebox at −80 °C for ~1 h, allowing complex inorganic salts to precipitate. Then, the solution was filtered in a vacuum at −80 °C, and the reference spectrum was taken. Then DTE (or 2-PhFu) stock solution was added, and the visible spectroscopic measurement was started. For the calculation of the apparent rate constant of the capping reaction, the concentration of *p*-ClSt-DTE$^+$ or *p*-ClSt-2-PhFu$^+$ carbenium ions was derived from the measured absorbance at the absorption maximum $\lambda_{max} = 467$ and 334 nm and the corresponding molar absorption coefficient $\epsilon_{max} = 44\,000$ L mol^{-1} cm^{-1} and $\epsilon_{max} = 30\,000$ L mol^{-1} cm^{-1} respectively[1] for DTE and 2-PhFu and path length $d = 0.02$ cm.

Results and Discussion

Living Cationic Polymerization of *p*-Chlorostyrene. Cationic polymerization of *p*-ClSt was carried out using the *p*-MeStCl/$TiCl_4$ initiating system; [*p*-ClSt] = 0.2 mol L^{-1}, [*p*-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1} in MeCHx/MeCl 60/40 (v/v) at −80 °C. The first-order plot of ln([M]$_0$/[M]) vs time and variation of M_n and PDI with conversion are shown respectively in Figures 1 and 2. The slope of the first-order plot was calculated to determine the apparent rate constant of propagation, $k_{app} = 8.95 \times 10^{-5}$ s^{-1}. The linear M_n−conversion plot together with the linear first-order plot indicates that in the polymerization of *p*-ClSt initiated with the *p*-MeStCl/$TiCl_4$ initiating system in MeCHx/MeCl 60/40 (v/v) solvent mixture at −80 °C chain transfer and termination are undetectable.

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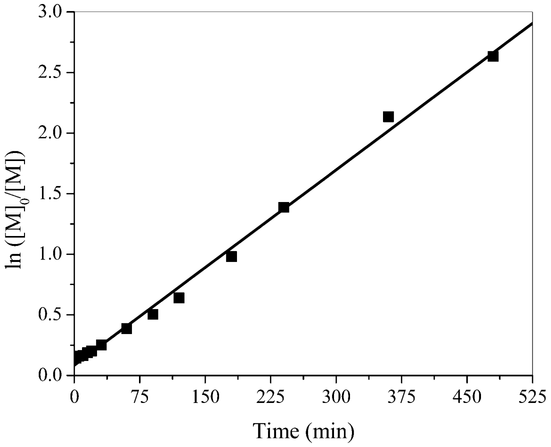


Figure 1. First-order plot of ln([M]$_0$/[M]) vs time for the polymerization of *p*-ClSt initiated by *p*-MeStCl/TiCl$_4$; [*p*-ClSt] = 0.2 mol L^{-1}, [*p*-MeStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [TiCl$_4$] = 0.036 mol L^{-1}, in MeCHx/MeCl 60/40 (v/v) at −80 °C.

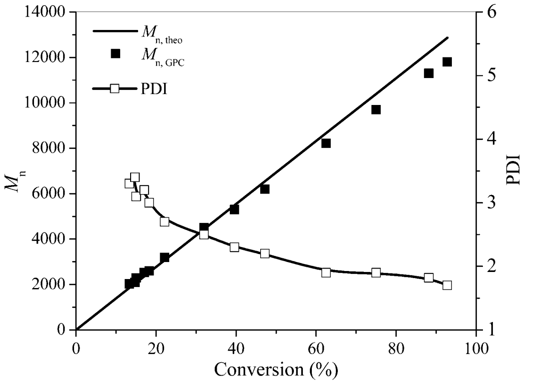


Figure 2. Variation of molecular weight (M_n) and molecular weight distribution (PDI) with conversion. Reaction conditions are the same as in Figure 1.

A control experiment, i.e., cationic polymerization of *p*-ClSt in the absence of initiator, *p*-MeStCl (direct initiation), was also carried out. Under the same conditions, 18.3% monomer conversion was obtained after 5 h. Thus, direct initiation is operational during the polymerization of *p*-ClSt initiated by *p*-MeStCl/TiCl$_4$, but it is much slower than in the presence of initiator and the kinetics of polymerization is unaffected.

In Figure 1, the first-order plot shows a positive intercept because of the different ionization rate constant of the initiator and the dormant polymer end. Recently, Storey et al.[13] reported that the average number of monomer units added per ionization−termination cycle, called the run number[14] ($RN = k_p^{\pm}[M]/k_{-i}$), can be determined by analysis of an initiation event they coined rapid monomer consumption (RMC). From RN and k_{app}, the apparent rate constants of ionization ($k_i^{app} = k_i^{abs}K_{D0}$, where k_i^{abs} is the absolute rate constant of ionization and K_{D0} is the equilibrium constant of TiCl$_4$ dimerization) can be calculated by the following equation:

$$k_{app} = k_p^{\pm}\frac{k_i^{app}}{k_{-i}}[I][TiCl_4]^2 = k_i^{app}\frac{RN}{[M]}[I][TiCl_4]^2 \quad (1)$$

where [I] is the initiator concentration, k_{-i} is the rate constant of deactivation (reversible termination), [M]$_0$ is the initial concentration of *p*-ClSt, and $k_p^{\pm}/k_{-i} = RN/[M]$. From the intercept of the first-order plot $RN = 8.1$ was calculated. From k_{app} and [I] = 0.002 mol L^{-1}, [M] = 0.2 mol L^{-1}, and [TiCl$_4$] = 0.036 mol L^{-1}, the k_i^{app} value of 0.85 L^2 mol^{-2} s^{-1} was obtained.

The *p*-ClStCl/TiCl$_4$ initiating system was then employed for polymerization of *p*-ClSt in MeCHx/MeCl 60/40 (v/v) solvent mixture at −80 °C. Figures 3 and 4 respectively show the first-order ln([M]$_0$/[M]) vs time plot and variation of M_n and PDI with conversion. The absence of a *y*-intercept in Figure 3, which is consistent with the RMC theory, predicts that an initiator that is structurally similar to the chain end will have a similar rate constant of ionization. The linear first-order plot indicates the absence of irreversible termination during the polymerization. From the slope of this plot $k_{app} = 6.1 \times 10^{-5}$ s^{-1} was obtained and indicates that the polymerization is a little slower with this initiating system compared to the *p*-MeStCl/TiCl$_4$ initiating system. A closer inspection of the first-order plots indicates that this difference could be due to errors in the last three data points in Figure 1. The molecular weights follow the theoretical M_n−conversion line, indicating the absence of chain transfer during the polymerization. These results shows that the polymerization of *p*-ClSt in the presence of DTBP in MeCHx/MeCl 60/40 (v/v) solvent mixture at −80 °C is living with both initiating systems.

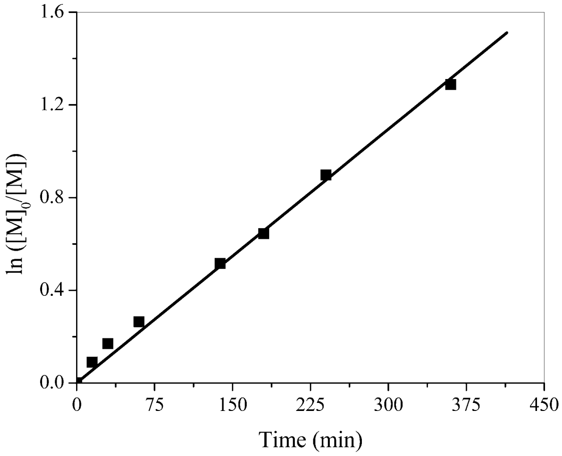


Figure 3. First-order plot of ln([M]$_0$/[M]) vs time for the polymerization of *p*-ClSt initiated by *p*-ClStCl/TiCl$_4$; [*p*-ClSt] = 0.2 mol L^{-1}, [*p*-ClStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [TiCl$_4$] = 0.036 mol L^{-1}, in MeCHx/MeCl 60/40 (v/v) at −80 °C.

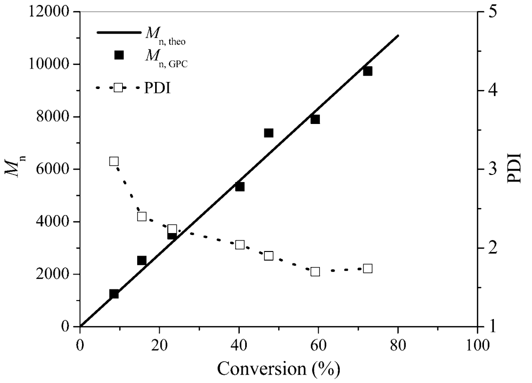


Figure 4. Variation of molecular weight (M_n) and molecular weight distribution (PDI) with conversion. Reaction conditions are the same as in Figure 3.

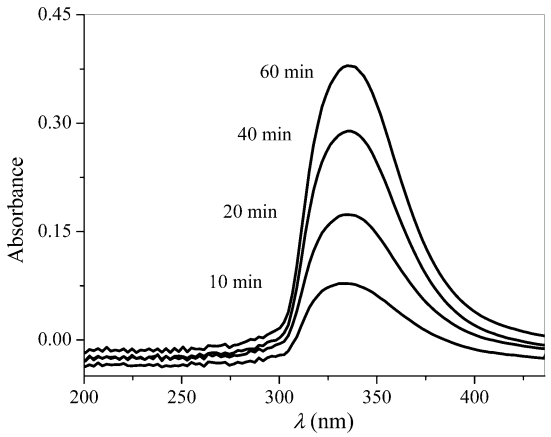


Figure 5. Selected UV−vis spectra measured during the capping reaction of *p*-ClStCl with 2-PhFu; [*p*-ClStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1}, and [PhFu] = 0.002 mol L^{-1} at −80 °C in MeCHx/MeCl 60/40 (v/v) solvent.

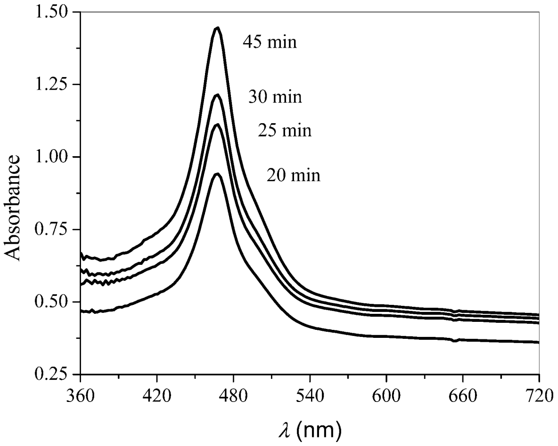


Figure 6. Selected UV−vis spectra measured during the capping reaction of *p*-ClStCl with DTE; [*p*-ClStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1}, and [DTE] = 0.005 mol L^{-1} in MeCHx/MeCl 60/40 (v/v) solvent at −80 °C.

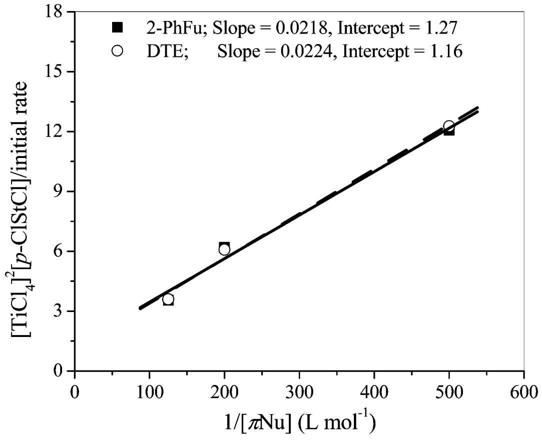


Figure 7. Plot of reciprocal initial rate of capping vs 1/[πNu] for the capping reaction of *p*-ClStCl with 2-PhFu (■) and DTE (○) in MeCHx/MeCl 60/40 (v/v) solvent mixture at −80 °C.

UV−Vis Spectroscopic Studies for the Capping Reaction of *p*-ClStCl with 2-PhFu and DTE. UV−vis studies were carried out for the calculation of apparent equilibrium constant of ionization ($K_i^{app} = K_i^{abs}K_{D0}$, where K_i^{abs} is the absolute equilibrium constant of ionization), k_i^{app}, and k_{-i} for the capping reaction of the model compound *p*-ClStCl with DTE or 2-PhFu under the following conditions: [*p*-ClStCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1} at −80 °C in MeCHx/MeCl 60/40 (v/v) solvent mixture. The concentrations of DTE and 2-PhFu were varied. The capping reaction was followed by measuring the absorption at $\lambda_{max} = 467$ and 334 nm for the capping reaction of *p*-ClStCl with DTE and 2-PhFu, respectively. Figures 5 and 6 show selected spectra, which were obtained during the capping reaction of *p*-ClStCl with 2-PhFu and DTE, respectively. The initial slope of the time-dependent evolution of the absorbance at $\lambda_{max} = 467$ nm and $\lambda_{max} = 334$ nm plot for the capping reaction of *p*-ClStCl with DTE and 2-PhFu, respectively, was used for the calculations.

The composite rate constant of capping, $k_cK_i^{app}$, and the apparent rate constant of ionization, k_i^{app}, have been determined using eq 2.[1]

$$\frac{[p\text{-ClStCl}][\text{TiCl}_4]^2}{\frac{d}{dt}([p\text{-ClSt-}\pi\text{Nu}^+\text{Ti}_2\text{Cl}_9^-] + [p\text{-ClSt-}\pi\text{Nu}^+])} = \frac{1}{k_cK_i^{app}[\pi\text{Nu}]} + \frac{1}{k_i^{app}} \qquad (2)$$

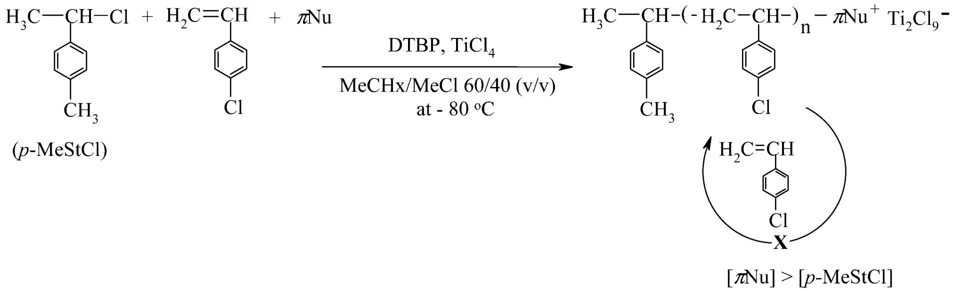
The denominator on the left side of eq 2 contains the sum of the concentrations of capped ion pairs and free ions, and [πNu] is the concentration of nonhomopolymerizable π-nucleophile (πNu). The plot of the left side of eq 2 vs 1/[πNu] should yield a straight line, with the slope and intercept of $1/k_cK_i^{app}$ and $1/k_i^{app}$, respectively. The plot is shown in Figure 7. From the known value of diffusion-controlled second-order rate constant $k_c = 3 \times 10^9$ L mol^{-1} s^{-1}, K_i^{app} and k_{-i}^{app} were calculated. From the intercept, $k_i^{app} = 0.82$ L^2 mol^{-2} s^{-1} was obtained at −80 °C, which is in excellent agreement with that of 0.85 L^2 mol^{-2} s^{-1} obtained from the analysis of RMC data. From the slope, $k_cK_i^{app} = 45$ L^3 mol^{-3} s^{-1} was obtained, which corresponds to $K_i^{app} = 1.5 \times 10^{-8}$ L^2 mol^{-2}. Using these K_i^{app} and k_i^{app}, $k_{-i} = 5.5 \times 10^7$ s^{-1} was calculated.

The K_i^{app} allows us to calculate the concentration of active chain ends, if we consider that the ionization constant of the dormant poly(*p*-ClSt) chain ends is similar to that of *p*-ClStCl. From the apparent rate constants of propagation for the living polymerization of *p*-ClSt and the concentration of active chain ends (determined from [*p*-ClStCl] = [*p*-MeStCl] = 0.002 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1} and K_i^{app}), the absolute rate constant of propagation for ion pairs, $k_p^{\pm} = 2.3 \times 10^9$ L mol^{-1} s^{-1} and 1.6×10^9 L mol^{-1} s^{-1}, were calculated respectively for the *p*-MeStCl/$TiCl_4$ and *p*-ClStCl/$TiCl_4$ initiating system at −80 °C in the MeCHx/MeCl 60/40 (v/v) solvent mixture. The small difference in $k_p^{\pm}$ could be due experimental errors in the apparent rate constants of propagation.

Competition Experiments. Competition experiments, i.e., polymerizations carried out in the presence of a capping agent,[1−5,15] were also used to determine $k_p^{\pm}$ in the carbocationic polymerization of *p*-ClSt (Scheme 1).

Since the capped chain ends are too stable to initiate polymerization, the polymerization stops when all chain ends are capped by the πNu. Both conversion and number-average degrees of polymerization reach a

Scheme 1. Competition Experiment with πNu



limiting value. Recently competition experiments have been successfully used to determine $k_p^\pm$ for the cationic polymerization of IB,[1,2] St,[3] p-MeOSt,[4] and TMeSt.[5] From the limiting conversion (x_∞) and number-average degree of polymerization ($DP_{n\infty}$), the reactivity ratio $k_p^\pm/k_c^\pm$ can be calculated using eqs 3 and 4.[1,2]

$$\frac{k_p^\pm}{k_c^\pm} = \frac{\ln(1 - x_\infty)}{\ln(1 - [p\text{-MeStCl}]_0/[\pi\text{Nu}]_0)} \tag{3}$$

$$\frac{k_p^\pm}{k_c^\pm} = \frac{\ln(1 - DP_{n\infty}[p\text{-MeStCl}]_0/[p\text{-ClSt}]_0)}{\ln(1 - [p\text{-MeStCl}]_0/[\pi\text{Nu}]_0)} \tag{4}$$

In eqs 3 and 4, $[p\text{-MeStCl}]_0$ is the initial concentration of the initiator, which equals that of the chain ends, $[\pi\text{Nu}]_0$ is the initial concentration of the capping agent, and $[p\text{-ClSt}]_0$ is the initial concentration of the monomer.

The polymerization of p-ClSt was carried out in the presence of either DTE or 2-PhFu as πNu with $TiCl_4$ as co-initiator at −80 °C in the MeCHx/MeCl 60/40 (v/v) solvent system and DTBP as proton trap. Limiting conversion was reached in 7 h, independent of the πNu used, regardless of whether DTE or 2-PhFu was used as capping agent. Direct initiation is operational in the competition experiments with DTE but much slower than the capping reaction, and the kinetics of capping is unaffected. 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 propagating cation and the absence of side reactions. The molecular weight distributions of the polymers were close to the most probable distribution ($M_w/M_n \approx 2$). The $k_p^\pm/k_c^\pm$ values were calculated from x_∞ using eq 3 and from $DP_{n,\infty}$ using eq 4. From the average values of $k_p^\pm/k_c^\pm$ for 2-PhFu and DTE $k_p^\pm = 3.3 \times 10^9$ and 2.7×10^9 L mol^{-1} s^{-1} were 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. 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.[2] The results of competition experiments are presented in Table 1. The $k_p^\pm$ values are in good agreement with those obtained from the online UV−vis spectroscopy; however, they are 7 orders of magnitude higher than previously reported values. The reasons for this large discrepancy between our k_p and reported k_p have been already discussed.[1,2]

Table 1. Limiting Conversion, Molecular Weight (M_n), Molecular Weight Distribution (PDI), and Absolute Propagation Rate Constants in the Competition Reactions of p-Chlorostyrene (p-ClSt) Polymerization with 1,1-Di-p-tolylethylene (DTE) or 2-Phenylfuran (2-PhFu) in MeCHx/MeCl 60/40 (v/v) at −80 °C[a]

πNu	conv (%)	M_n (GPC)	PDI	$k_p^\pm/k_c^\pm$(conv)	$k_p^\pm/k_c^\pm$(M_n)	$k_p^\pm \times 10^{-9}$ (L mol^{-1} s^{-1})
DTE	24.2	3340	1.9	1.1	1.1	3.3
2-PhFu	19.4	2840	1.9	0.86	0.91	2.7

[a] $[p\text{-MeStCl}] = 0.002$ mol L^{-1}, $[TiCl_4] = 0.036$ mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, $[p\text{-ClSt}] = 0.2$ mol L^{-1}, [DTE] = [2-PhFu] = 0.009 mol L^{-1}.

In conclusion, living cationic polymerization of p-ClSt was attained by both the p-MeStCl/$TiCl_4$ and p-ClStCl/$TiCl_4$ initiating system in the MeCHx/MeCl 60/40 (v/v) solvent mixture at −80 °C. Analyzing RMC data, run number and the apparent rate constant of ionization, k_i^{app}, have been determined for p-ClSt polymerization. UV−vis spectroscopic measurements allowed the determination of kinetic parameters for the capping reaction of p-ClStCl with DTE or 2-PhFu in the MeCHx/MeCl 60/40 (v/v) solvent mixture at −80 °C. Under the same conditions, the K_i^{app} value for p-ClStCl is almost 8.5 times lower than the value determined for StCl, which explains the lower rate of polymerization for p-ClSt compared to St. The $k_i^{app} = 3.97$ and 0.85 L^2 mol^{-2} s^{-1} and $k_{-i} = 3.25 \times 10^7$ and 5.5×10^7 s^{-1} values, which were obtained under identical conditions for StCl and p-ClStCl, respectively, indicate that, as expected, the styryl cation is more stable than the p-ClSt cation. On the basis of competition experiments and UV−vis spectroscopic measurements, the propagation step in the cationic polymerization of p-ClSt is essentially diffusion limited.

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