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Structure−Reactivity Scales in Carbocationic Polymerizations

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ABSTRACT: The polymerization of *p*-methylstyrene (*p*MeSt) in the presence of isobutylene (IB), styrene (St), *p*-chlorostyrene (*p*ClSt), and 1,3-butadiene (BD) was carried out at −40 °C. By selecting CH_2Cl_2/methylcyclohexane (MeCHx) 50/50 (v/v) solvent mixture and the appropriate weak Lewis acid, $SnBr_2Cl_2$ monoaddition of IB, St, *p*ClSt, and BD followed by instantaneous termination was achieved, and the polymerizations stopped short of completion. The reactivity ratios, k_p/k_{12}, where k_p is propagation rate constant and k_{12} is the cross-propagation rate constant, were calculated on the basis of limiting conversions and limiting molecular weights. According to these values, *p*MeSt is 3.8 ± 0.5, 4.8 ± 1.1, 7.2 ± 1.6, and 100 ± 6 times more reactive than IB, St, *p*ClSt, and BD respectively. Similar competition reactions between IB/BD, St/BD, and *p*ClSt/BD in conjunction with $TiCl_4$ as Lewis acid yielded $k_p/k_{12} = 77 \pm 5$, 7.1 ± 1.0, and 3.2 ± 0.7, respectively. Using k_p/k_{12} and k_p for *p*MeSt, St, and *p*ClSt, the cross-propagation k_{12} values were calculated to establish structure−reactivity scales. Similarly to our earlier observations, comparison of these values indicated that structural differences have a much larger effect on cation reactivity than on monomer reactivity.

Introduction

Recently, we have reported on a reaction clock method for the determination of the cross-propagation rate constant using conditions (Lewis acid, temperature, solvent polarity) where cationic copolymerizations terminate after a single cross-propagation; i.e., the reaction (Scheme 1) of P_1^+ with M_2 results in the exclusive formation of [1:1] adduct (terminating copolymerization) followed by irreversible trapping of cation with halide.[1−3] This is feasible when crossing over from the more reactive to the less reactive monomer. Under these conditions the cross-propagation rate constant k_{12} can be calculated from the reactivity ratio $r_1 = k_p/k_{12}$ using the known value of the propagation rate constant k_p for M_1. The value of r_1 could be determined from the limiting conversion or limiting number-average degree of polymerization. The corresponding equations have been derived and reported previously.[4,5] A comparison of the k_{12} values for different monomers against a standard polymer cation yields the scale of monomer reactivity while the comparison of k_{12} values for different polymer cations against a standard monomer gives a scale of cation reactivity.[2] To date, we have studied the relative reactivities of C-4 olefins toward the polyisobutylene cation (PIB^+)[1] and the relative reactivities of IB, *p*MeSt, St, and *p*ClSt against the poly(*p*-methoxystyryl) cation ($PpMeOSt^+$).[2]

In this paper we report on relative reactivity of IB, *p*ClSt, St, and BD toward the poly(*p*-methylstyryl) cation ($PpMeSt^+$) and on the relative reactivity of $PpMeSt^+$, PIB^+, poly(styryl) (PSt^+), and poly(*p*-chlorostyryl) cation ($PpClSt^+$) toward BD.

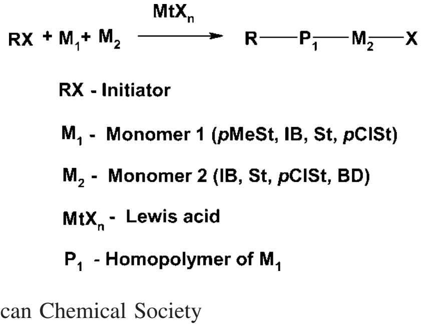
Experimental Section

Materials. IB was dried in the gaseous state by passing it through in-line gas-purifier columns packed with BaO/drierite. IB and BD (Aldrich, 99%) were condensed in the cold bath of a glovebox prior to polymerization. Tin tetrachloride ($SnCl_4$, 99.9%), tin tetrabromide ($SnBr_4$, 99%), titanium tetrachloride ($TiCl_4$, 99.9%), and DTBP (97%) were purchased from Aldrich and used as received. Tin dibromodichloride ($SnBr_2Cl_2$) was prepared by mixing a 1:1 molar ratio of $SnBr_4$ and $SnCl_4$. The *p*MeSt (Aldrich, 96%), St (Aldrich, 97%), and *p*ClSt (Aldrich, 99%) were freed from inhibitor by washing with 5% aqueous NaOH solution followed by distilled water until neutral. After drying (or passing) over anhydrous Na_2SO_4, the styrenic monomers were distilled from CaH_2 under reduced pressure and stored under nitrogen at −20 °C, and they were distilled once again from CaH_2 under reduced pressure prior to use. The 1-chloro-1-(4-methylphenyl)ethane (*p*MeStHCl) initiator was synthesized by a procedure reported earlier.[5,6] The CH_2Cl_2 was washed with 5% aqueous NaOH solution and then with distilled water until neutral. Then it was predried on anhydrous Na_2SO_4 and distilled from CaH_2 under nitrogen. This distilled CH_2Cl_2 was refluxed under nitrogen overnight with phosphorus pentoxide (P_2O_5) and distilled to a round-bottom flask containing P_2O_5. It was refluxed under nitrogen overnight and distilled just before use. Methylcyclohexane (MeCHx) was refluxed over CaH_2 overnight under nitrogen and distilled before use. Tetrahydrofuran (reagent grade, Aldrich) was refluxed on CaH_2 under a nitrogen atmosphere for 24 h and distilled before use. Methanol (reagent grade, Doe & Ingals) was distilled.

Polymerization. Polymerizations were carried out under a dry nitrogen atmosphere in an MBraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). Large (75 mL) culture tubes were used as polymerization reactors. The total volume of the reaction mixture was 15 mL. After predetermined times the polymerizations were quenched by the addition of 1.0 mL of prechilled methanol. All polymers were purified by reprecipitation from CH_2Cl_2/methanol twice. Monomer conversions were determined by gravimetric analysis.

Competition. In a typical competition experiment into a 75 mL culture tube calculated amounts of CH_2Cl_2 or CH_2Cl_2/MeCHx, DTBP, and *p*MeStHCl stock solutions, *p*MeSt, and the terminating monomer (IB, BD, St, or *p*ClSt) were added and mixed thoroughly

Scheme 1. Schematic Description of Competition Reaction



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and cooled to −40 °C. The polymerization was started by the addition of precooled solution of $SnCl_4$ or $SnBr_2Cl_2$ in CH_2Cl_2 or CH_2Cl_2/MeCHx. After a predetermined polymerization time 1.0 mL of prechilled methanol was introduced to quench the polymerization. These polymers were purified by dissolution and reprecipitation using CH_2Cl_2 and methanol twice. Conversions were measured using gravimetric analysis after drying the polymers to constant weight under vacuum. Competition reactions with IB/BD, St/BD, and *p*ClSt/BD were carried out in a similar way using $TiCl_4$ as co-initiator.

Characterization. Molecular weights were measured with a Waters GPC system equipped with a model 515 HPLC pump, a model 410 differential refractometer, a Viscostar viscometer (Wyatt Technology Inc.), a model 2847 dual λ absorbance detector, an online multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), a model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 mL/min at room temperature. NMR spectroscopy was carried out on a Bruker 500 MHz spectrometer using $CDCl_3$ as a solvent (Cambridge Isotope Laboratory, Inc.). ^1H NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane as internal standard (δ_H 0.00). The matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF MS) measurements were performed with a Waters/Micromass mass spectrometer equipped with a TOF analyzer. The positive ions were detected in linear mode. The polymer samples (10 mg/mL) in THF were prepared with a dithranol matrix (20 mg/mL in THF). To produce cations, sodium trifluoroacetate (NaTFA) dissolved in THF at a concentration of 1 mg/mL was added to the matrix/analyte solution. The solutions were mixed in 10:2:1 volume ratio (matrix:analyte: salt). A volume of 0.5 μL of these solutions was deposited onto the target plate (stainless steel) and allowed to air-dry, and the MALDI-TOF mass spectra were recorded.

Determination of Rate Constants. Reactivity ratios were determined from the limiting conversion (x_∞) or limiting number-average degree of polymerization ($DP_{n\infty}$) using eqs 1 and 2, where $[I]_0$ is the initial concentration of the initiator, which equals that of the chain ends, and $[M_2]_0$ and $[M_1]_0$ are the initial concentration of monomers. The value of k_{12} was calculated from k_p/k_{12} and k_p.

$$\frac{k_p}{k_{12}} = \frac{\ln(1 - x_\infty)}{\ln(1 - [I]_0/[M_2]_0)} \tag{1}$$

$$\frac{k_p}{k_{12}} = \frac{\ln(1 - DP_{n\infty}[I]_0/[M_1]_0)}{\ln(1 - [I]_0/[M_2]_0)} \tag{2}$$

Results and Discussion

Competition Experiments of *p*MeSt with IB, St, and *p*ClSt Using *p*MeStHCl/$SnCl_4$. Experimentation started with the *p*MeStHCl/$SnCl_4$/CH_2Cl_2/−40 °C system reported for the living polymerization of *p*MeSt that was utilized for the determination of k_p.[6] As expected, the polymerizations stopped short of completion, and limiting conversions were reached in 30 min under these conditions (Figure S1 and Table S1). MALDI-TOF MS analysis of low molecular weight samples, however, indicated monoaddition only with IB, while polymers obtained from competition experiments with St and *p*ClSt showed multiple additions. Multiple St or *p*ClSt additions at the chain end will not affect the kinetic evaluation; however, due to the concentration difference between *p*MeSt and St or *p*ClSt, it is more likely that these are isolated units, and thus eqs 1 and 2 are not valid.

We have reported earlier that the rate of ion collapse can be increased, and hence multiple addition of terminating monomer can be suppressed by decreasing the solvent polarity and Lewis acid strength or by increasing the temperature.[2,7,8] First the living polymerization of the *p*MeSt was demonstrated using *p*MeStHCl/$SnCl_4$ at a reduced polarity in CH_2Cl_2/MeCHx (50/50, v/v) at −40 °C by constructing the first-order plots and the M_n−conversion plots (Figure S2). These results indicated that termination and chain transfer are undetectable. MALDI-TOF MS analysis of the polymers obtained from the competition experiments under these conditions showed monoaddition of IB; however, with St and *p*ClSt multiple addition was still visible along with the monoaddition product.

Table 1. Limiting Conversion, Molecular Weight, and k_p/k_{12} Values in the Competition Reactions between *p*MeSt and IB[a]

solvent	[IB] (mol L^{-1})	conv (%)	M_n (GPC)	PDI	k_p/k_{12} (conv)	k_p/k_{12} ($DP_{n\infty}$)	k_p/k_{12} (av)
CH_2Cl_2	0.01	53.0	6300	1.6	3.4	3.4	3.4
CH_2Cl_2	0.02	34.2	4400	1.8	3.9	4.4	4.2
CH_2Cl_2/MeCHx (50/50, v/v)	0.01	51.9	6100	1.4	3.3	3.2	3.3
CH_2Cl_2/MeCHx (50/50, v/v)	0.02	37.2	4400	1.7	4.4	4.4	4.4

[a] [*p*MeSt] = 0.2 mol L^{-1}; [*p*MeStHCl] = 0.002 mol L^{-1}; [DTBP] = 0.006 mol L^{-1}; [$SnCl_4$] = 0.02 mol L^{-1}, time = 30 min (CH_2Cl_2), 300 min (CH_2Cl_2/MeCHx (50/50, v/v)) at −40 °C.

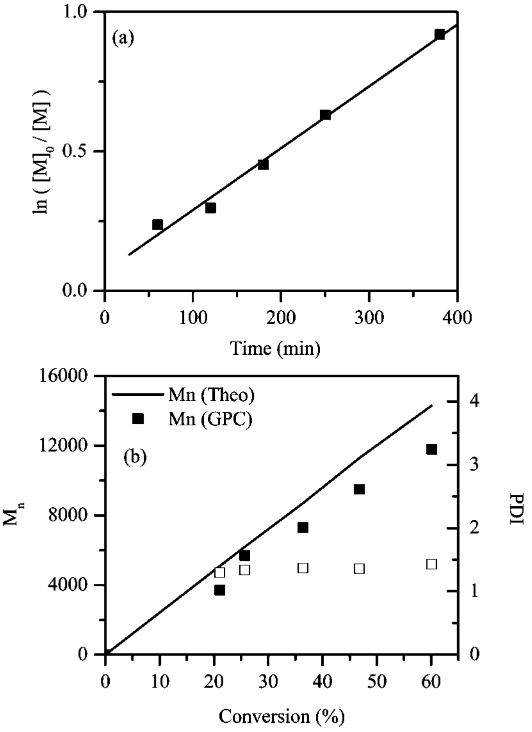

Figure 1. (a) First-order plot of $\ln([M]_0/[M])$ vs time and (b) variation of M_n and PDI with conversion for cationic polymerization of *p*MeSt initiated by *p*MeStHCl/$SnBr_2Cl_2$ in CH_2Cl_2/MeCHx (50/50, v/v) at −40 °C; [*p*MeSt] = 0.2 mol L^{-1}; [*p*MeStHCl] = 0.001 mol L^{-1}; [DTBP] = 0.006 mol L^{-1}; [$SnBr_2Cl_2$] = 0.36 mol L^{-1}.

The reactivity ratios determined using the limiting conversions and number-average degree of polymerizations for IB are listed in Table 1.

Polymerization in CH_2Cl_2/MeCHx (50/50, v/v) with $SnBr_2Cl_2$. Since multiple additions of St and *p*ClSt could not be prevented even at a reduced solvent polarity, further experiments were carried out with $SnBr_2Cl_2$, a weaker Lewis acid compared to $SnCl_4$. First the living polymerization of *p*MeSt was studied in CH_2Cl_2/MeCHx (50/50, v/v) at −40 °C. The first-order plot and the M_n and the polydispersity index (PDI) vs conversion plots are shown in Figure 1a,b. The first-order plot of $\ln[M_0]/[M]$ vs time is linear but shows a small positive intercept similar to earlier observations.[6] The M_n vs conversion plot is also linear starting at the origin, although the observed molecular weights are slightly lower than the theoretical values.

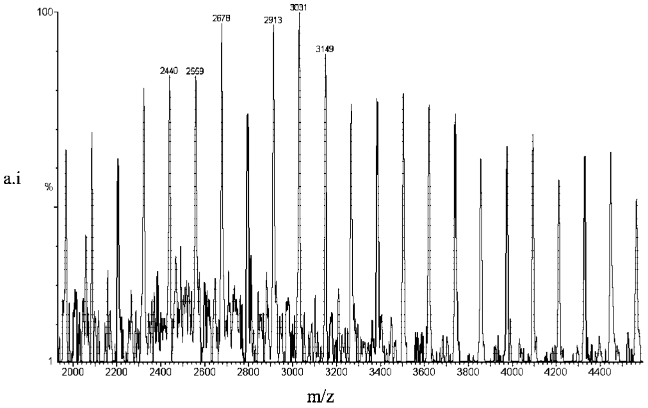

Figure 2. MALDI-TOF MS spectrum of P*p*MeSt-IB-Cl prepared using [*p*MeStHCl] = 0.001 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [$SnBr_2Cl_2$] = 0.36 mol L^{-1}, and CH_2Cl_2/MeCHx (50/50, v/v).

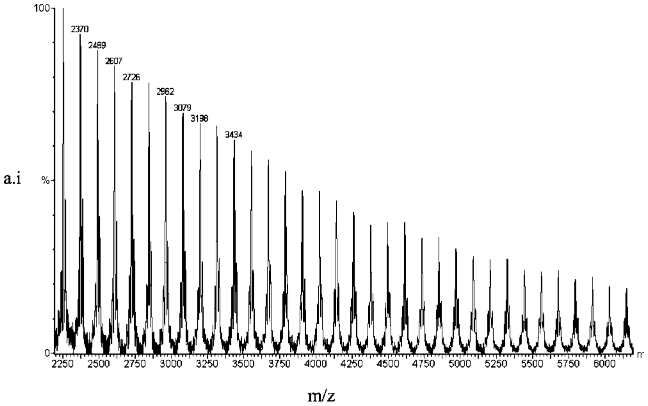

Figure 3. MALDI-TOF MS spectrum of P*p*MeSt-St-Cl prepared using [*p*MeStHCl] = 0.001 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [$SnBr_2Cl_2$] = 0.36 mol L^{-1}, and CH_2Cl_2/MeCHx (50/50, v/v).

Under these conditions competition experiments were carried out at low *p*MeSt concentration to obtain low molecular weight samples, which were analyzed by MALDI-TOF MS. Figures 2−4 show representative spectra of samples obtained in the competition experiments with IB, St, and *p*ClSt.

Monoaddition is confirmed when the mass of each peak in the MALDI-TOF MS can be described by eq 3, where *I* is the mass of the initiator residue, *n* is the number of repeat units, M_{M1} and M_{M2} are the molecular weights of M1 and M2 monomers, and Na^+ is the mass of sodium cation. The factor −1 is due to hydrogen halide elimination from the halide-terminated polymer ends under MALDI conditions. Figures 2−4 confirm monoaddition not only with IB but also with St and *p*ClSt under these conditions.[9]

$$M = I + nM_{M1} + M_{M2} - 1 + Na^+ \qquad (3)$$

Competition Experiments of *p*MeSt with IB, St, and *p*ClSt Using *p*MeStHCl/$SnBr_2Cl_2$. All polymerizations stopped short of completion, and a limiting conversion was achieved in 720 min. From the limiting conversions and number-average degrees of polymerizations the reactivity ratios were determined, and the values are listed in Table 2. The M_ns obtained from GPC are in good agreement with the theoretical M_n assuming one polymer chain is formed from one molecule of initiator. The polydispersity indices of these polymers were in the range of 1.7−1.9.

According to Table 2, *p*MeSt is 3.8 ± 0.5, 4.8 ± 1.1, and 7.2 ± 1.6 times more reactive than IB, St, and *p*ClSt in CH_2Cl_2/MeCHx (50/50, v/v) at −40 °C.

Table 2. Limiting Conversion, Molecular Weight, and k_p/k_{12} Values in the Competition Reactions[a]

M_2	[M_2] (mol L^{-1})	conv (%)	M_n (GPC)	PDI	k_p/k_{12} (conv)	k_p/k_{12} ($DP_{n\infty}$)	k_p/k_{12} (av)
IB	0.005	50.8	12200	1.7	3.2	3.3	3.3
IB	0.01	36.7	8800	1.8	4.3	4.3	4.3
St	0.0075	42.3	9000	1.8	3.9	3.4	3.7
St	0.015	35.3	7100	1.9	6.3	5.2	5.8
*p*ClSt	0.0125	36.7	9000	1.9	5.5	5.7	5.6
*p*ClSt	0.025	29.6	7100	1.9	8.6	8.8	8.7

[a] [*p*MeSt] = 0.2 mol L^{-1}; [*p*MeStHCl] = 0.001 mol L^{-1}; [DTBP] = 0.006 mol L^{-1}; [$SnBr_2Cl_2$] = 0.36 mol L^{-1}, time = 720 min, in CH_2Cl_2/MeCHx (50/50, v/v) at −40 °C.

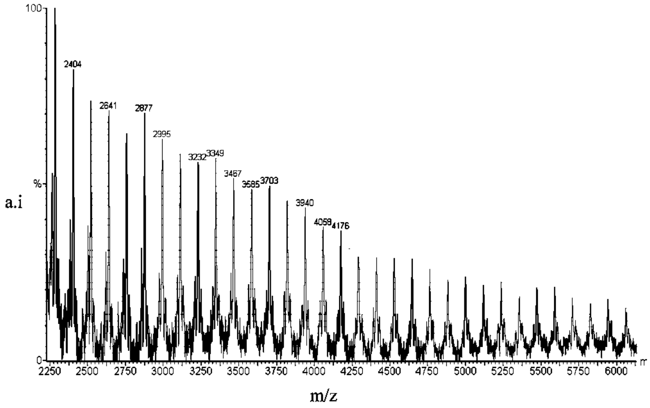

Figure 4. MALDI-TOF MS spectrum of P*p*MeSt-ClSt-Cl prepared using [*p*MeStHCl] = 0.001 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [$SnBr_2Cl_2$] = 0.36 mol L^{-1}, and CH_2Cl_2/MeCHx (50/50, v/v).

Comparison of Reactivity Ratios with Published Values. In the copolymerization of *p*MeSt with IB using $TiCl_4$ at −90 °C, $r_{pMeSt} = 10 \pm 4$ in *n*-butyl chloride and $r_{pMeSt} = 8 \pm 3$ in ethyl chloride were reported by Kennedy and co-workers.[10] Our r_{pMeSt} values in Table 2 are somewhat lower possibly due to the different temperature and solvent polarity.

Hallpap and co-workers[11] reported $r_{pMeSt} = 4.25$ in the copolymerization of *p*MeSt and St, in close agreement with our values. Higashimura and co-workers reported $r_{pMeSt} = 2.48 \pm 0.09$ in the copolymerization of *p*MeSt with St using WCl_6 in benzene at 30 °C,[12] which is lower than the value we report in this paper possibly due to the higher temperature of polymerization. Using $AcClO_4$ in different solvents (CH_2Cl_2 or CH_2Cl_2/CCl_4 or $C_6H_5NO_2$) at 0 °C another publication reported $r_{pMeSt} = 1.8 - 3.2$.[12] Sigwalt and co-workers reported $r_{pMeSt} = 2.49$ and 6.64 in the copolymerization of *p*MeSt with St and *p*ClSt, respectively, in CH_2Cl_2 at −10 °C.[13] Similar values (r_{pMeSt} = 2.5 and 6.6) were published by Wood et al.[14] Kennedy and co-workers[15] found $r_{pMeSt} = 4.5$ in the copolymerization of *p*MeSt and *p*ClSt in CCl_4 at 0 °C. These values are in reasonable agreement with the value reported in this report.

Competition Experiments of *p*MeSt, IB, St, and *p*ClSt with BD. In our previous paper[2] comparison could only be made between the reactivity of P*p*MeOSt$^+$ and PIB$^+$ cations based on the k_{12} values for IB. Comparison for PSt$^+$, P*p*ClSt$^+$ cations would require determination of k_{12} values for a standard monomer of low reactivity since these cations are highly reactive and add reactive monomers at a diffusion limited rate. Addition rate constants of BD to PIB$^+$ have already been reported.[1] According to these results, BD is a good candidate since it is about 64 times less reactive than IB in CH_3Cl/Hex 50/50, (v/v) at −40 °C. First, competition experiments were carried out with *p*MeSt/BD, St/BD, and *p*ClSt/BD. For the competition studies between BD and *p*MeSt, the following conditions were used: [*p*MeSt] = 0.2 mol L^{-1}, [*p*MeStHCl] = 0.001 mol L^{-1},

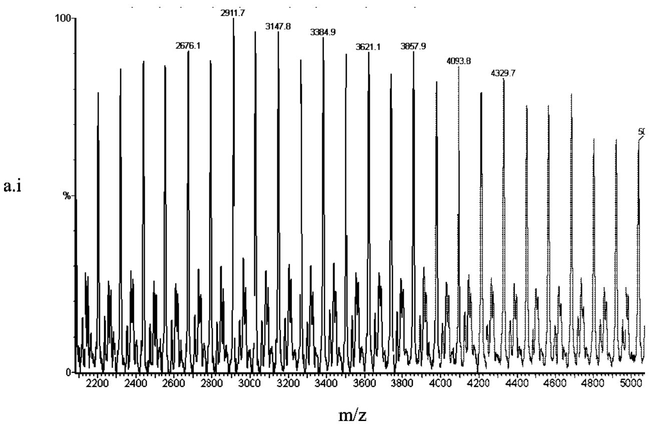

Figure 5. MALDI-TOF MS spectrum of P*p*MeSt-BD-Cl prepared using [*p*MeStHCl] = 0.001 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [$SnBr_2Cl_2$] = 0.36 mol L^{-1}, and CH_2Cl_2/MeCHx (50/50, v/v).

Table 3. Limiting Conversion, Molecular Weight, and k_p/k_{12} Values in the Competition Reactions between *p*MeSt, St, and *p*ClSt toward BD[a]

M_1	[BD] (mol L^{-1})	conv (%)	M_n (GPC)	PDI	k_p/k_{12} (conv)	k_p/k_{12} ($DP_{n\infty}$)	k_p/k_{12} (av)
*p*MeSt	0.15	47.4	11 000	1.7	96	94	95
*p*MeSt	0.3	29.3	7 200	1.7	104	109	106
IB	0.15	41.7	19 500	1.7	81	64	72
IB	0.3	25.1	12 900	1.6	86	78	82
St	0.01	51.5	10 900	1.9	6.9	5.4	6.1
St	0.02	35.5	7 500	2.0	8.5	7.7	8.1
*p*ClSt	0.005	45.4	12 000	1.3	2.71	2.39	2.5
*p*ClSt	0.001	34.4	8 900	1.4	4.0	3.66	3.8

[a] [*p*MeSt] or [St] or [*p*ClSt] = 0.2 mol L^{-1}; [*p*MeStHCl] = 0.001 mol L^{-1}; [DTBP] = 0.006 mol L^{-1}; [$SnBr_2Cl_2$] = 0.36 mol L^{-1}, or [$TiCl_4$] = 0.72 mol L^{-1}, in CH_2Cl_2/MeCHx = 50/50 (v/v) at −40 °C.

[$SnBr_2Cl_2$] = 0.36 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, and [BD] = 0.3 mol L^{-1}. For the competition experiments with St/BD and *p*ClSt/BD, $TiCl_4$ (0.72 mol L^{-1}) was used as co-initiator. Living polymerization of St and *p*ClSt was established by constructing the diagnostic plots (Figures S3 and S4) using *p*MeStHCl/$TiCl_4$ in CH_2Cl_2/MeCHx (50/50, v/v) at −40 °C. ^{1}H NMR analysis of all the polymers obtained in the competition experiments (Figures S5−S7) showed the absence of C*H*−Cl chain end protons at ~4.4 ppm and the presence of olefinic protons at ~5.5 and 5.3 ppm and $-CH{=}CHCH_2Cl$ signal at 3.8 ppm indicating quantitative crossover.

Figures 5 and 6 show the MALDI-TOF MS of the product obtained in the *p*MeSt/BD and St/BD competition. By deducting the initiator residue, the molecular weight of the repeat units and sodium cation, a residue of 54 amu was calculated, which corresponds to one BD unit per chain.[9] In agreement with previous reports,[2,16] HCl elimination was observed under MALDI-TOF MS conditions. Attempts to obtain the MALDI-TOF MS of P*p*ClSt-BD-Cl were unsuccessful.

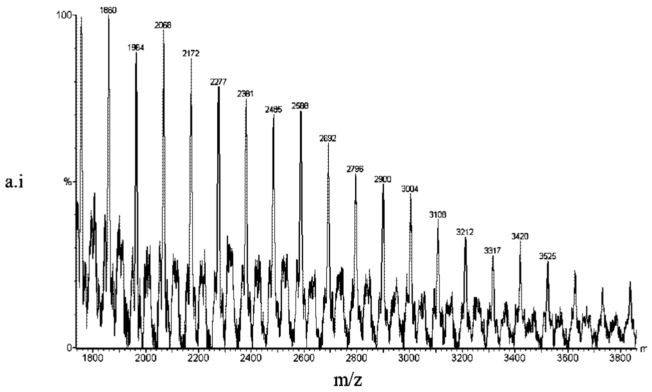

Figure 6. MALDI-TOF MS spectrum of *p*MeStH-PSt-BD-Cl prepared using [*p*MeStHCl] = 0.001 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [$TiCl_4$] = 0.72 mol L^{-1}, and CH_2Cl_2/MeCHx (50/50, v/v).

Detailed competition studies (Figures S8−S10) were performed with *p*MeSt/BD, IB/BD, St/BD, and *p*ClSt/BD to determine the reactivity ratios in CH_2Cl_2/MeCHx (50/50, v/v) at −40 °C using $SnBr_2Cl_2$ or $TiCl_4$ as co-initiator. Limiting conversions were achieved after 720, 180, 300, and 900 min for *p*MeSt/BD, IB/BD, St/BD, and *p*ClSt/BD, respectively. From the limiting conversions and the limiting degree of polymerizations the reactivity ratios listed in Table 3 were calculated. According to Table 3, BD is about 100 ± 6, 77 ± 5, 7.1 ± 1.0, and 3.2 ± 0.7 times less reactive than *p*MeSt, IB, St, and *p*ClSt, respectively. These data would suggest that IB is about 11 times more reactive than St, in contrast to data in Table 2, which suggest similar reactivities. However, when k_p is diffusion limited as in the case in the polymerization of St and *p*ClSt, the reactivity ratios only provide a lower limit.

Competition experiments were also performed between *p*MeOSt and BD to determine the reactivity ratios, but crossover from *p*MeOSt to BD was not observed and limiting conversions were not achieved even with 5.0 mol L^{-1} of BD due to large reactivity difference between *p*MeOSt and BD.

Comparison of Monomer Reactivities Based on k_p/k_{12} Values with the Nucleophilicity Parameters. The nucleophilicity (N) parameters $N_{pMeSt} \approx 1.70$ (approximate number), $N_{IB} = 1.11$, $N_{St} = 0.78$, $N_{pClSt} \approx 0.21$ (approximate number), and $N_{BD} = -0.87$ have been reported by Mayr.[17,18] According to these values, *p*MeSt is 3.9, 8.3, 31, and 370 times more reactive than IB, St, *p*ClSt, and BD, respectively, at 20 °C. Similarly, IB is 100 times more reactive than BD, while St and *p*ClSt are 45 and 12 times more reactive than BD. From the competition reactions, *p*MeSt is 3.8 ± 0.5, 4.8 ± 1.1, 7.2 ± 1.6, and 100 ± 6 times more reactive than IB, St, *p*ClSt, and BD, respectively, in CH_2Cl_2/MeCHx (50/50, v/v) at −40 °C and BD is 77 ± 5, 7.1 ± 1.0, and 3.2 ± 0.7 times less reactive than IB, St, and *p*ClSt. While the monomer reactivity follows the order *p*MeSt > IB > St > *p*ClSt > BD by both methods there are two reasons why the absolute reactivities by the two methods differ somewhat. First, the temperatures are different, and a change in temperature may affect the reactivity ratios when the activation enthalpies for homopropagation and cross-propagation

Table 4. Rate Constants (L mol^{-1} s^{-1}) for Cation−Monomer Reactions in CH_2Cl_2/MeCHx (50/50, v/v) at −40 °C

	polymer cation				
monomer	P*p*MeOSt$^+$	P*p*MeSt$^+$	PIB$^+$	PSt$^+$	P*p*ClSt$^+$
*p*MeOSt	7800	diffusion limited	diffusion limited	diffusion limited	diffusion limited
*p*MeSt	186	3×10^{8}[a]	diffusion limited	diffusion limited	diffusion limited
IB	29	**7.9×10^{7}**	7×10^{8}[b]	diffusion limited	diffusion limited
St	26	**6.2×10^{7}**		diffusion limited (4×10^{9})	diffusion limited
*p*ClSt	10	**4.2×10^{7}**			diffusion limited (3×10^{9})
BD		**3×10^{6}**	**9.1×10^{6}**[c]	**5.6×10^{8}**	**9.4×10^{8}**

[a] Estimated value from $k_p = 1 \times 10^9$ L mol^{-1} s^{-1} in CH_2Cl_2. [b] Value from Hex/MeCl (50/50). [c] Value calculated from $k_p = 7 \times 10^8$ L mol^{-1} s^{-1} in Hex/MeCl (50/50, v/v).

are different. Even more importantly, when the homopropagation rate constant is close to the diffusion limit, competition experiments only give a lower limit for the reactivity ratio as pointed out above. For instance, according to the *N* parameters St is 45 times more reactive than BD; however, competition experiments gave $r_{St} = 7.1 \pm 1.0$, since propagation of St is diffusion limited.

Comparison of Monomer and Cation Reactivity. The cross-propagation rate constant (k_{12}) values presented in Table 4 were calculated using the reactivity ratios and the propagation rate constants (k_p) in CH_2Cl_2/MeCHx (50/50, v/v) at −40 °C. Table 4 contains results from the present study (in bold) and earlier reported[1,2] values in the same solvent mixture and temperature. Since cation reactivities are independent of the nature of Lewis acid,[8] comparison between the k_{12} values can be made without regard to the counteranions.

In Table 4 monomer reactivities can be compared against a standard cation in any vertical column. The data in any horizontal row provide the order of cation reactivities against a standard monomer. As discussed in the previous section, when the rate constants reach the diffusion limit, quantitative comparison cannot be made. According to our previous report with respect to P*p*MeOSt$^+$, *p*MeSt is 6.4, 7.1, and 18.6 times more reactive than IB, St, and *p*ClSt under similar conditions. Based on the data in the third column of Table 4, *p*MeSt is 3.8 ± 0.5, 4.8 ± 1.1, and 7.2 ± 1.6 times more reactive than IB, St, and *p*ClSt. As discussed in the previous section, when the rate constants reach the diffusion limit, quantitative comparison cannot be made. Thus, the reactivity of St compared to BD is underestimated based on column 5; in contrast, data in column 3 suggest that St is more than 20 times more reactive than BD.

The relative reactivity of various carbocations can also be analyzed by comparing the data in each row. On the basis of previously published data in Table 4, we reported that substituents have a much larger effect on the cation reactivity than on the monomer reactivity. For instance, the P*p*MeOSt$^+$ cation is about 10^6 times less reactive compared to the P*p*MeSt$^+$ cation, while *p*MeOSt is only 42 times more reactive than *p*MeSt. We find similar differences in cation reactivity between the P*p*MeOSt$^+$ and P*p*MeSt$^+$ cation against IB, St, or *p*ClSt as a standard monomer. Against BD (last row of Table 4) the P*p*MeSt$^+$ cation is 187 and 313 times less reactive than PSt$^+$ and P*p*ClSt$^+$, while the difference between the reactivity of the corresponding monomers is much smaller.

Conclusions

Monoaddition of IB, St, *p*ClSt, and BD to P*p*MeSt$^+$ and of BD to PSt$^+$ and P*p*ClSt$^+$ could be accomplished by careful selection of the experimental conditions. Cross-propagation rate constants determined from the competition reactions could be used to extend the structure−reactivity scales for monomers and carbocations. In line with the conclusions of our previous report, structural differences have a much larger effect on the cation reactivity than on the monomer reactivity.

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Supporting Information Available: First-order plots, ^{1}H NMR spectra of BD-capped polymers, and detailed results of competition experiments for M_n, PDI, and limiting conversion in CH_2Cl_2/MeCHx at −40 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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