1724 *Macromolecules* **2010**, *43*, 1724–1729
DOI: 10.1021/ma902488m

Macromolecules
ARTICLE

Structure−Reactivity Scales in Carbocationic Polymerizations: The Case of α-Methylstyrene

Philip Dimitrov and Rudolf Faust*

*Polymer Science Program, Department of Chemistry, University of Massachusetts Lowell,
1 University Avenue, Lowell, Massachusetts 01854*

Received November 9, 2009; Revised Manuscript Received January 10, 2010

ABSTRACT: The propagation rate constant, k_p, for the cationic polymerization of α-methylstyrene (αMeSt) was determined. First, the polymerization of αMeSt was carried out initiated by the diα−MeStHCl/SnBr$_4$ initiator/coinitiator system in dichloromethane (DCM) or in DCM/methylcyclohexane (MeCHx) 1:1 (v/v) solvent mixture at −80 °C in the presence of allyltrimethylsilane (ATMS). Clean and quantitative addition of ATMS to the propagating end terminates the polymerization, and from the limiting conversion and molecular weights, the k_p/k_{ATMS} ratio was calculated. The $k_p = (5.2 \text{ and } 7.7) \times 10^7$ L mol^{-1}s^{-1} in DCM and DCM/MeCHx 1:1 (v/v), respectively, were calculated from the k_{ATMS} values determined by the diffusion clock method. Competition polymerizations between αMeSt and each of the following monomers *p*-methylstyrene (*p*MeSt), isobutylene (IB), styrene (St), and *p*-chlorostyrene (*p*ClSt) were performed in DCM/MeCHx 1:1 (v/v) at −80 °C. From the limiting conversions and molecular weights, the reactivity ratios k_p/k_{12} were determined. A comparison of the k_{12} values for different monomers against a standard polymer cation and that for different polymer cations against a standard monomer indicated that the effect of substituents on carbocation reactivity is much larger than their effect on monomer reactivity.

Introduction

The cationic polymerization of α-methylstyrene (αMeSt) has been known for at least a half century.[1] Several attempts have been made to determine the rate constant of propagation (k_p) for αMeSt from the polymerization rate and the ionic species concentration (ISC), and the resulting k_p values vary from 2×10^4 to 4×10^6 L mol^{-1} s^{-1}.[2] Such significant differences in the k_p values determined by the ISC method were also observed for other monomers.[3]

In the past few years, we have reported on the utilization of the reaction clock method to determine k_p in the carbocationic polymerization of isobutylene (IB),[4] styrene (St),[5] and ring-substituted styrenes.[6−9] The reaction clock method references the unknown rate constant for the reaction of the intermediate cation to that for a second reaction with a known rate constant, which serves as a "clock". In the diffusion clock method, the "clock" speed is the diffusion limit.[10] In general, we have employed simple competition experiments to determine k_p. In these experiments, polymerizations, which proceed in the absence of chain transfer and conventional termination, were carried out in the presence of π-nucleophiles or hydride donors, which terminate the chains by forming a stable cation or a cation that can rapidly eliminate a cationic fragment (e.g., Me$_3$Si$^+$), or by hydride transfer. Therefore, the cationic polymerization of monomer M$_1$ with a terminating nucleophile M$_2$ results in limiting conversions of M$_1$.[6−12] The terminating nucleophile M$_2$ can also be addressed as a capping agent because all of the polymeric chains have M$_2$ or a fragment from M$_2$ as an end group. From the limiting conversion (x_∞) or from the corresponding limiting number-average degree of polymerization (DP$_\infty$), the reactivity ratio, k_p/k_c, can be calculated from the following relationships

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

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

where k_p is the rate constant of propagation for M$_1$ and k_c is the rate constant of capping, $[I]_0$ 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 concentrations of the capping agent and the monomer, respectively.[6] When k_c is known (diffusion limited or separately determined), k_p can be calculated.[6] Most of our reported competition experiments have been carried out under conditions where the active centers were paired ions, and thus propagation rate constants for ion pairs ($k_p^{\pm}$) were determined. However, competition experiments under different conditions to yield unpaired ions resulted in very similar propagation rate constants for free ions (k_p^{+}), and thus differentiation between the two k_p values is unnecessary.

We have recently extended our studies to terminating copolymerizations, which terminate after a single cross-propagation. We have shown that this is feasible with a suitable Lewis acid when crossing over from a more reactive monomer to a less reactive one, where rapid and irreversible ion collapse terminates the propagating chain. Equations 1 and 2 are also valid for this case, and when k_p is known, the cross-propagation rate constant (k_{12}) can be calculated. A comparison of the k_{12} values for different monomers against a standard polymer cation yields the scale of monomer reactivity, whereas the comparison of k_{12} values for different polymer cations against a standard

---

*Corresponding author. E-mail: Rudolf_Faust@uml.edu.

monomer gives a scale of cation reactivity. To date, we have studied the relative reactivity of: (1) C-4 olefins toward the polyisobutylene cation (PIB^+), (2) IB, *p*-methylstyrene (*p*MeSt), St, and *p*-chlorostyrene (*p*ClSt) against the poly(*p*-methoxystyryl) cation ($PpMeOSt^+$), (3) IB, *p*ClSt, St, and 1,3-butadiene (BD) toward the poly(*p*-methylstyryl) cation ($PpMeSt^+$), and (4) $PpMeSt^+$, PIB^+, poly(styryl) (PSt^+), and poly(*p*-chlorostyryl) cation ($PpClSt^+$) toward BD. The results indicated that substituents have a much larger effect on the cation reactivity than on the monomer reactivity.

The goals of the present study are (a) to determine k_p for the cationic polymerization of αMeSt and (b) to extend our structure−reactivity relationship to αMeSt and $P\alpha MeSt^+$.

Experimental Section

Materials. Technical grade hexanes (Dow & Ingals) were refluxed over H_2SO_4 for 48 h, then washed with 5% KOH aqueous solution, and then washed with water. Hexanes were predried with anhydrous Na_2SO_4 and then stirred over CaH_2 under high vacuum for at least 24 h. Hexanes were collected by vacuum distillation into an ampule with Teflon stopcock connected to the high vacuum line. Methylcyclohexane (MeCHx) was stirred over CaH_2 for 24 h under high vacuum, and then it was vacuum distilled into another ampule before use. Dichloromethane (DCM) was freed from stabilizers first by washing it with 5% NaOH and then with water. Then, it was predried with anhydrous Na_2SO_4 and then stirred over CaH_2 at high vacuum for 24 h and cryodistilled under high vacuum into an ampule containing P_2O_5, where DCM was stirred for at least 24 h before distilling it for use.

Tin tetrabromide ($SnBr_4$, Aldrich, 99%), 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 97%), allyltrimethylsilane (ATMS, Gelest), methallytrimethylsilane (MATMS, Gelest), 1-(trimethylsiloxy)cyclopentene (TMSOCP, Aldrich, 97%), and 2,4-diphenyl-4-methyl-1-pentene (diαMeSt, Aldrich, 97%) were used as received. IB (Matheson Tri Gas) gas was dried by passing it through in-line gas-purifier columns packed with BaO/Drierite and then condensed in a receiver flask at −80 °C before use. Styrenic monomers αMeSt (Aldrich, 99%), *p*MeSt (Alfa Aesar, 98%), St (Aldrich, 99%), and *p*ClSt (Aldrich 97%) were washed with 5% aqueous NaOH solution, followed by distilled water until neutral. After drying over anhydrous Na_2SO_4, monomers were distilled from CaH_2 under reduced pressure prior to use. Hydrochlorinated diαMeSt (diαMeStHCl) was synthesized in a similar way to a previously reported procedure by bubbling of dry HCl gas into diαMeSt in dry hexanes at −78 °C for 2 h.[13] The reaction mixture was purged with dry nitrogen at −78 °C for 30 min to remove excess HCl. White crystals of diαMeStHCl were washed three times with prechilled hexanes at −80 °C before use.

Competition Polymerization Procedures. Competition polymerizations were carried out under a dry N_2 atmosphere in a MBraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). Screw-top culture tubes (75 mL) were used as polymerization reactors and were immersed in heptane bath thermostatted at −80 °C. A calculated amount of prechilled solvents and stock solutions of the reagents were added to the culture tube, and the polymerization was started by the addition of a stock solution of the $SnBr_4$ in DCM. The total volume of the polymerization mixture was 15 mL. After predetermined time, the polymerization was terminated by the addition of 1 mL of prechilled methanol. Polymers were recovered by reprecipitation from DCM/methanol. Monomer conversions were determined gravimetrically.

Competition Reactions. Competition reactions between ATMS, MATMS, and TMSOCP toward $Di\alpha MeStH^+$ were performed in the same glovebox setup as that described above. First, at −80 °C, the two competing reagents (overall concentration equal or larger than 0.2 M) and diαMeStHCl (0.02 M) were mixed together with the solvent (overall volume 15 mL) in a 75 mL culture tube. The competition reaction was started with the addition of a stock solution of $SnBr_4$ of 0.01 M final concentration in DCM or 0.02 M when the reaction was performed in DCM/MeCHx 1:1 (v/v). After 2 h, the reaction was terminated with 10 mL of aqueous ammonia, and the products were recovered from the lower organic layer.

Characterization. *SEC*. Absolute molecular weights and polydispersities of the polymers were obtained by size exclusion chromatography using a Waters 712 WISP autosampler, 515 HPLC pump, 410 differential refractometer, 441 UV−vis detector, a MiniDawn multi angle laser light scattering (MALLS) detector (44.7, 90.0, and 135.4° measurement angles) (Wyatt Technology Inc.), ViscoStar viscosity detector (Wyatt Technology Inc.), and five Ultrastyragel GPC columns connected in the following order: 500, 10^3, 10^4, 10^5, and 100 Å. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min^{-1} at room temperature. Results were processed by Astra 5.3 software (Wyatt Technology Inc.) using universal calibration.

Nuclear Magnetic Resonance. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker 500 MHz spectrometer using $CDCl_3$ as a solvent (Cambridge Isotope Lab., Inc.).

MALDI-TOF. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF MS) measurements were performed on a Micromass M@LDI MALDI-TOF MS (Waters Corp.) equipped with a 337 nm N_2 laser. Positive ions were detected in the linear mode using an accelerating voltage of 15 kV and low laser frequency. Mass spectra from 50 shots were accumulated to produce a final spectrum. Samples were prepared similarly as in ref 14 by using THF as a solvent. Polymer sample solutions (10 g L^{-1}, 30 μL) were mixed together with NaTFA solution (10 g L^{-1}, 30 μL) and dithranol matrix solution (30 g L^{-1}, 90 μL), and 0.5 μL of the mixed solution was deposited onto a target plate well.

Results and Discussion

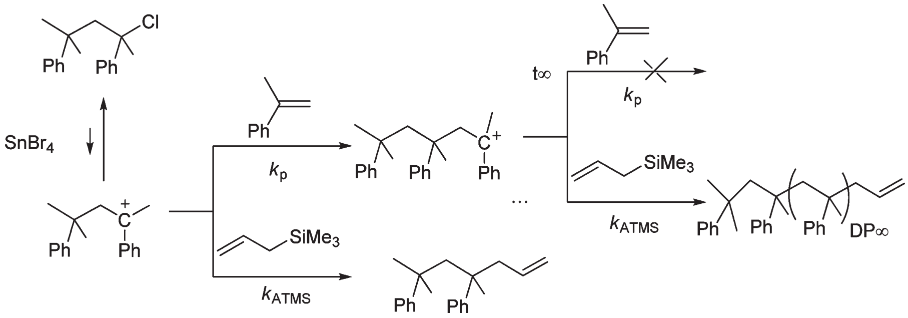
Determination of k_p for the Cationic Polymerization of αMeSt. *Competition Reactions between αMeSt and ATMS toward $P\alpha MeSt^+$*. Competition experiments that stop short of completion require a nucleophile or a capping agent with an appropriate reactivity. The rate constant for a given nucleophile−electrophile combination can be addressed by the following relationship

$$\log k_{20C} = s(N + E) \qquad (3)$$

where k_{20C} is the rate constant at 20 °C, N is nucleophilicity parameter, E is electrophilicity parameter, and s is a nucleophile specific constant, in many cases close to unity.[20]

Nucleophiles with too high or too low reactivity will yield too low or too high monomer conversions of αMeSt, respectively, from which reliable reactivity ratios cannot be determined. Although the monomer concentrations can be varied, the concentration of the terminating nucleophile must be higher than the concentration of initiator, and, in general, it should be low enough not to affect the polarity of the solution. Therefore, finding a suitable nucleophile is of key importance. Allylsilanes are appealing as terminating nucleophiles because they are readily available, generally react with cations quantitatively, and exhibit reactivities that span a wide range depending on the substituents. Experimentation with many allylsilanes suggested that ATMS is a suitable nucleophile. Polymerizations of αMeSt in the presence of ATMS were performed at −80 °C in DCM or in a DCM/MeCHx 1:1 (v/v) mixed solvent system at the following concentrations: [αMeSt] = 0.2 M, [ATMS] = 0.02 to 0.04 M, [diαMeStHCl] = 0.001 to 0.002 M, [$SnBr_4$] = 0.008 to 0.02 M,

Scheme 1. Competition Polymerization of αMeSt and ATMS



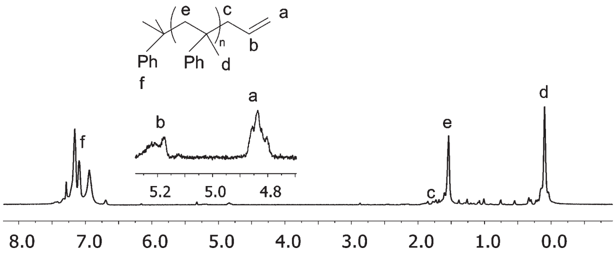


Figure 1. ^{1}H NMR spectrum in $CDCl_3$ of the reaction product of competition polymerization of ATMS and αMeSt under the following conditions: [αMeSt] = 0.2 M; [ATMS] = 0.04 M, [diαMeStHCl] = 0.002 M; [DTBP] = 0.006 M; [$SnBr_4$] = 0.008 M, DCM, −80 °C.

and [DTBP] = 0.006 M. The living polymerization of αMeSt coinitiated with $SnBr_4$ (Figure S1 of the Supporting Information) has already been reported in DCM or in the mixed solvent under the similar conditions.[19] ATMS is a weaker nucleophile (nucleophilicity parameter, $N = 1.79$) compared with αMeSt ($N = 2.35$)[20] and formed the allyl-terminated adduct quantitatively in a model reaction with diαMeStH$^+$ (Figure S4 of the Supporting Information). The competition reaction with αMeSt is presented in Scheme 1. The data from the competition polymerizations are collected in Tables S1 and S2 of the Supporting Information. Quantitative 1:1 addition of the allyl group from ATMS to PαMeSt$^+$ was shown by ^{1}H NMR spectroscopy (Figure 1) and MALDI-TOF MS (Figure 2). From eqs 1 and 2, $k_p/k_{ATMS} = 7$ in DCM and 15 in DCM/MeCHx 1:1 (v/v) were determined.

Competition Reactions between ATMS and MATMS, MATMS and TMSOCP, and ATMS and TMSOCP toward diαMeStH$^+$. To derive the k_p of αMeSt from the k_p/k_{ATMS} ratio, we must first determine the cross-propagating constant k_{ATMS}. The reaction of diαMeStH$^+$, generated by complete ionization of diαMeStHCl with excess $TiCl_4$, with ATMS, however, was too fast, and the decrease in diαMeStH+ concentration with time could not be observed by conventional UV−vis spectroscopy.[15] Therefore, the diffusion clock method was chosen for the determination of k_{ATMS} (Scheme 4). Competition reactions were performed under the same conditions as those for the competition polymerization of αMeSt with ATMS, except at a higher [diαMeStHCl] = 0.02 M. Model reactions of MATMS and TMSOCP with diαMeStH$^+$ also showed quantitative and clean addition (Figures S3 and S2, respectively, of the Supporting Information). The molar fractions of the products from the competition reactions were determined by ^{1}H NMR spectroscopy. The results are summarized in Table 1. Detailed results are presented in Tables S3, S4, and S5 of the Supporting Information.

Competition reactions involving ATMS and MATMS were previously used for the determination of k_p for the cationic polymerization of IB[10] and St.[7] MATMS ($N = 4.41$) is a ~1000 times more reactive nucleophile than ATMS ($N = 1.79$) toward carbocations of low electrophilicity.[20] In the reaction with diαMeStH$^+$ (Scheme 2), which is a much weaker electrophile compared with PIB$^+$ and PSt$^+$, MATMS was ~100 times more reactive than ATMS (Table S3 of the Supporting Information), and k_{MATMS} might not be diffusion-limited.

TMSOCP ($N = 6.57$) is ~150 times more reactive than MATMS toward carbocations of low electrophilicity ($E < 2$).[20a] Because competition experiments showed TMSOCP to be ~3 times more reactive than MATMS ($k_{TMSOCP}/k_{MATMS} = 2.5$ in DCM and 3.1 in DCM/MeCHx 1:1) toward diαMeStH$^+$ (Scheme 3), one can conclude that k_{TMSOCP} is diffusion-limited.[17] In line with this conclusion, the correlation $\log k = s(E + N)$ yields a second-order rate constant of 3×10^{11} L mol^{-1} s^{-1} for the reaction of TMSOCP with cumyl cation ($E = 5.74$)[21] at 20 °C, which is already beyond the diffusion limit. The diffusion-limited second-order rate constant was previously set arbitrarily to 3×10^9 L mol^{-1} s^{-1} for hexane/methylchloride (Hex/MeCl 1:1 v/v) at −80 °C, at which $\eta = 0.778$ mPa s. For DCM at −80 °C, a higher dynamic viscosity of 1.42 mPa s was calculated from existing data.[18] By applying Walden's rule,[6] ($D\eta$ = constant, where D is the diffusion coefficient) k_{TMSOCP} was determined to be 1.9×10^9 L mol^{-1} s^{-1} in DCM. For DCM/MeCHx 1:1 at −80 °C, $\eta = 1.93$ mPa s was estimated, and in this case, $k_{TMSOCP} = 1.4 \times 10^9$ L mol^{-1} s^{-1}.

The rate constant of addition of diαMeStH$^+$ to ATMS was calculated from competition experiments with TMSOCP and ATMS (Scheme 4) and by combining the ratios k_{TMSOCP}/k_{MATMS} and k_{MATMS}/k_{ATMS}. The values determined by both competition experiments were in a good agreement, giving an average value $k_{ATMS} = 7 \times 10^6$ L mol^{-1} s^{-1} in DCM and 5×10^6 L mol^{-1} s^{-1} in DCM/MeCHx (Table 1). This number is in excellent agreement with the rate constant of 1.2×10^7 L mol^{-1} s^{-1} measured for the reaction of αMeStH$^+$ with ATMS in DCM at 20 °C.[21] Because of the highly negative value of the entropy of activation, this rate constant can be assumed to be temperature-independent.[20e,f] From the k_{ATMS} values, for the cationic polymerization of αMeSt, $k_p = 5.2 \times 10^7$ L mol^{-1} s^{-1} in DCM and 7.7×10^7 L mol^{-1} s^{-1} in DCM/MeCHx 1:1 (v/v) at −80 °C were calculated. This is almost identical to the rate constant of 1.2×10^8 L mol^{-1} s^{-1} calculated for the addition of the cumyl cation to αMeSt by Ammer and Mayr in this issue.[21]

Determination of k_p/k_c Ratios for *p*MeSt, St, IB, and *p*ClSt by Competition Polymerization with αMeSt. To compare the relative reactivity of αMeSt with other styrenic monomers and IB, polymerizations of αMeSt were performed in DCM/MeCHx 1:1 (v/v) at −80 °C in the presence of *p*MeSt, IB, St,

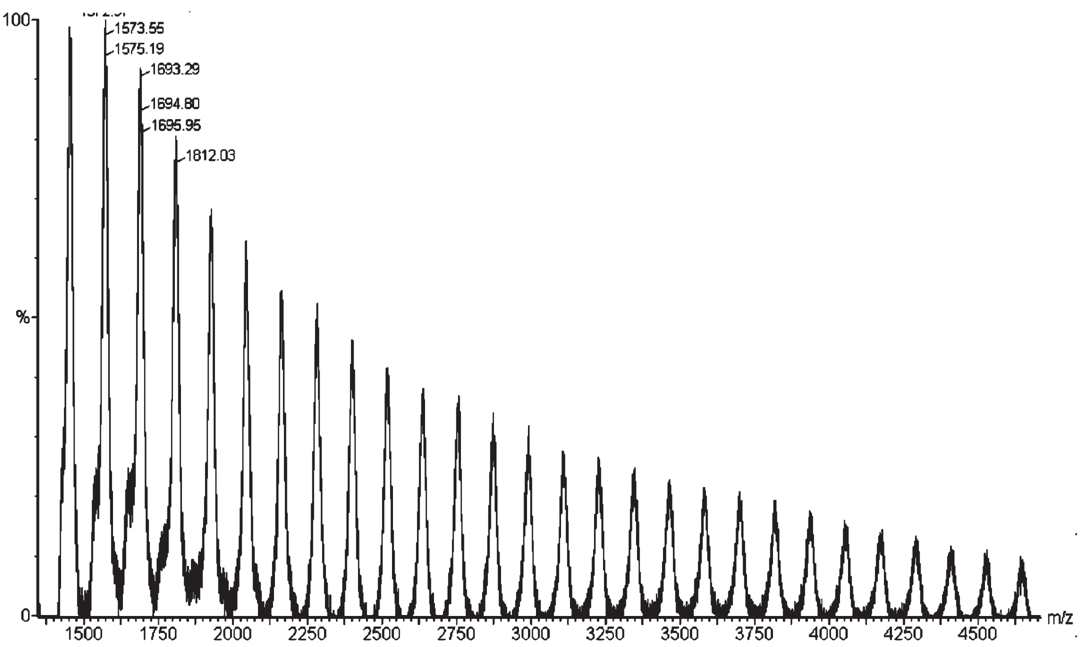


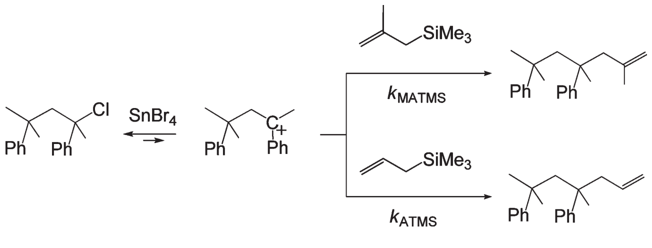
Figure 2. MALDI-TOF MS of PαMeSt capped with ATMS.

Table 1. Competition Reactions between ATMS and MATMS, MATMS and TMSOCP, and ATMS and TMSOCP toward diMeSt$^+$ Performed at −80 °C

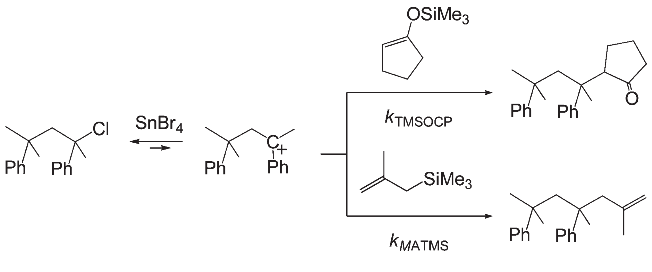
solvent	k_p/k_{ATMS}	k_{TMSOCP}/k_{ATMS}	k_{TMSOCP}/k_{MATMS}	k_{MATMS}/k_{ATMS}	$k_{ATMS}{}^a$ (L mol^{-1} s^{-1})	$k_{ATMS}{}^b$ (L mol^{-1} s^{-1})	$k_p{}^a$ (L mol^{-1} s^{-1})	$k_p{}^b$ (L mol^{-1} s^{-1})	$k_p{}^c$ (L mol^{-1} s^{-1})
DCM	7	225	2.5	114	8.4×10^6	6.6×10^6	5.8×10^7	4.6×10^7	5.2×10^7
DCM/MeCHx	15	255	3.1	95	5.4×10^6	4.7×10^6	8.1×10^7	7.3×10^7	7.7×10^7

[a] Calculated from k_{TMSOCP}/k_{ATMS} ratio where $k_{TMSOCP} = 1.9 \times 10^9$ L mol^{-1} s^{-1} in DCM and $k_{TMSOCP} = 1.4 \times 10^9$ L mol^{-1} s^{-1} in DCM/MeCHx 1:1. [b] Calculated from k_{TMSOCP}/k_{MATMS} and k_{MATMS}/k_{ATMS} ratio where $k_{TMSOCP} = 1.9 \times 10^9$ L mol^{-1} s^{-1} in DCM and $k_{TMSOCP} = 1.4 \times 10^9$ L mol^{-1} s^{-1} in DCM/MeCHx 1:1. [c] Average value from k_p from a and b.

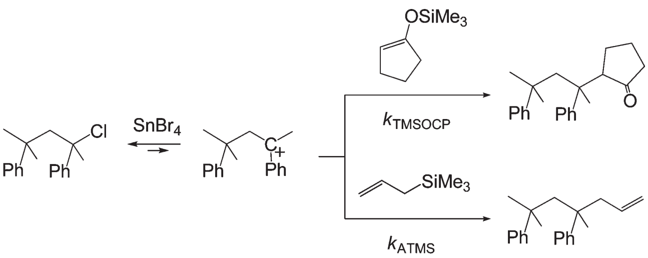
Scheme 2



Scheme 3



Scheme 4



or *p*ClSt. A relatively weak Lewis acid $SnBr_4$ was used because it is unable to ionize the chain ends capped with *p*MeSt, IB, St, or *p*ClSt. The results are presented in Table 2. The ^{1}H NMR spectrum of the IB-capped sample showed the resonances characteristic for exo-olefin end group, resulting from dehydrobromination (Figure S6 of the Supporting Information). The characteristic resonance expected for $-\mathrm{C\underline{H}}-$Br was also absent from the ^{1}H NMR spectra of PαMeSt capped with styrenic monomers (Figures S5, S6, and S7 of the Supporting Information) suggesting dehydrobromination (clearly seen in Figure S7 of the Supporting Information). Attempts to obtain MALDI-TOF MS spectra were unsuccessful most likely because of the decomposition of PαMeSt under MALDI conditions.

Evaluation of Monomer Reactivities Determined by Competition Polymerizations and Comparison with Previously Established Nucleophilicity Parameters. Previously determined *N* parameters under standard conditions for αMeSt, *p*MeSt, IB, St, and *p*ClSt are 2.35,[20b] 1.70,[20a] 1.11,[20a] 0.78,[20a] and 0.20,[20c] respectively. Therefore, for standard conditions, αMeSt appears to be 5, 17, 37, and 141 times more reactive than *p*MeSt, IB, St, and *p*ClSt, respectively, toward carbocation of low electrophilicity ($E < 6$) if the same value of *s* from

Table 2. Competition Polymerizations of αMeSt with *p*MeSt, IB, St, and *p*ClSt[a]

no.	Nu	[Nu]	time	yield	Mn	Mn	M_w/M_n	$k^{\pm}_p/k_c$	$k^{\pm}_p/k_c$	$k^{\pm}_p/k_c$
		(M)	(min)	(%)	(theor)	(SEC)		(yield)	(DP)	(avg)
1	*p*MeSt[b]	0.05	240	19	4593	5500	1.80	11	13	13
2	*p*MeSt[b]	0.05	360	23	5433	5500	2.25	13	13	
3	IB	0.20	120	39	6003	6200	1.48	63	67	69
4	IB	0.20	240	46	7058	5500	2.00	78	58	
5	IB	0.20	360	46	7067	5700	2.12	78	60	
6	St	0.40	120	44	6749	5400	1.90	147	113	196
7	St	0.40	240	57	8847	8600	1.74	218	214	
8	St	0.40	360	51	7929	7300	2.03	185	168	
9	*p*ClSt	2.00	120	42	6555	6000	2.01	709	646	717
10	*p*ClSt	2.00	240	44	6826	6000	2.10	749	646	
11	*p*ClSt	2.00	360	49	7670	6200	2.25	881	674	

[a] [diαMeStHCl] = 0.00155 M, [αMeSt] = 0.02 M, [$SnBr_4$] = 0.02 M, DCM/MeCHx 1:1 (v/v), −80°C. [b] [diαMeStHCl] = 0.001 M.

Table 3. Rate Constants (L mol^{-1} s^{-1}) for Cation/Monomer Reactions in DCM/MeCHx (1:1 v/v) at −40°C

monomer	polymer cation					
	P*p*MeOSt+[12]	PαMeSt+	P*p*MeSt+[12]	PIB+[12]	PSt+[12]	P*p*ClSt+[12]
*p*MeOSt	7.8×10^3	DL[a]	DL	DL	DL	DL
αMeSt		7.7×10^7[b]	DL	DL	DL	DL
*p*MeSt	1.9×10^2	5.9×10^6	3.0×10^8[c]	DL	DL	DL
IB	2.9×10^1	1.1×10^6	7.9×10^7	7.0×10^8[d]	DL	DL
St	2.6×10^1	3.9×10^5	6.2×10^7		DL	DL
*p*ClSt	1.0×10^1	1.1×10^5	4.2×10^7			DL
BD			3.0×10^6	9.1×10^6	5.6×10^8	9.4×10^8

[a] DL is abbreviation for diffusion limited. [b] Determined at −80 °C in DCM/MeCHx (1:1 v/v). [c] Estimated value from $k_p = 1 \times 10^9$ in DCM. [d] Value from hexanes/methylchloride (1:1 v/v).

eq 3 is assumed for these reactions. From competition polymerizations performed at −80 °C, αMeSt is 13, 69, 196, and 717 times more reactive than *p*MeSt, IB, St, and *p*ClSt, respectively. A similar difference was previously observed[16] and can be explained by the different temperature effect on the rates of propagation and cross-propagation because of the higher activation enthalpies of the latter. The reactivity of *p*MeSt is 4, 8, and 31 times higher than IB, St, and *p*ClSt, respectively, as determined from the *N* parameters, and from competition experiments at −80 °C, *p*MeSt is 5, 15, and 55 times more reactive than the same monomers toward $P\alpha MeSt^+$, which is in fairly good agreement. If we compare the relative monomer reactivity toward another polymer cation, P*p*MeOSt$^+$ (Table 3), then *p*MeSt is 6, 7, and 19 times more reactive than IB, St, and *p*ClSt, which is also in accord with the values obtained in the current study.

Comparison Cation and Monomer Reactivity and Effect of Substituent. The cross-propagation rate constants previously determined and from the present study are listed in Table 3. Monomer reactivities can be compared against a standard polymer cation in any of the vertical columns. The cross-propagation rate constants of a standard monomer (horizontal rows) provide the scale of cation reactivity. P*p*ClSt$^+$ is the least stable cation because of the electron-withdrawing effect of the Cl group; therefore, it is the most reactive cation in the investigated series. Against BD (last row), P*p*ClSt$^+$ is two times more reactive than PSt^+, which may be underestimated because BD adds to P*p*ClSt$^+$ at close to the diffusion limit. PSt^+ is 62 times more reactive than PIB^+ and ~200 times more reactive than P*p*MeSt$^+$, which reflects the electron-donating effect of the methyl group. The BD row ends here because P*p*MeOSt$^+$ and $P\alpha MeSt^+$ are too unreactive against BD. The rows of *p*MeSt, IB, St, and *p*ClSt complete the comparison for the less reactive cations P*p*MeSt$^+$, $P\alpha MeSt^+$, and P*p*MeOSt$^+$. Therefore, by combining the BD row and, for instance, the *p*ClSt row, further comparisons can be made. Therefore, P*p*MeSt$^+$ is ~380 times more reactive than $P\alpha MeSt^+$, which is ~10 000 times more reactive than P*p*MeOSt$^+$. From the combination of the data in these two rows, P*p*ClSt$^+$ is 1 billion times more reactive than P*p*MeOSt$^+$, whereas the reactivity of *p*MeOSt is only ~800 times higher than that of *p*ClSt. Similarly, P*p*MeSt$^+$ is 50−400 times more reactive than $P\alpha MeSt^+$, whereas αMeSt is only 13 times more reactive than *p*MeSt. It should be noted here that such differences in reactivities only become effective when diffusion-controlled processes are excluded.

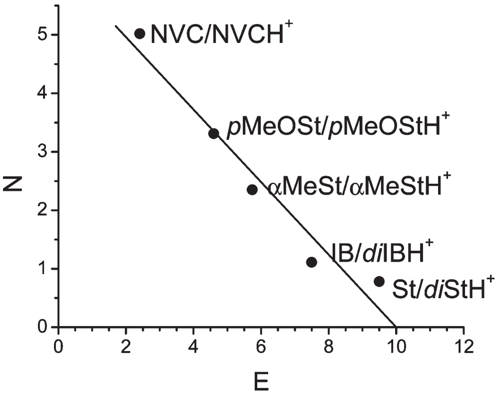


Figure 3. *N*−*E* correlation for some cationically polymerizable monomers and their corresponding cations. *N* parameters for *N*-vinyl carbazole (NVC), *p*MeOSt, αMeSt, IB, St, and were determined in refs 20d, 20e, 20b, 20g, and 5, respectively. The *E* parameters for the corresponding $NVCH^+$, *p*MeOStH$^+$, $\alpha MeStH^+$, *di*IBH$^+$, and *di*StH$^+$ were determined in refs 20d, 20e, 21, 20g, and 5, respectively.

The *E* versus *N* plot (Figure 3) shows that with increasing monomer reactivity, the reactivity of the corresponding cation decreases. The *E* parameters in Figure 3 are for monomeric cations for NVC, *p*MeOSt, and αMeSt and for dimeric IB and St cations. However, the *E* parameter changes only slightly from monomeric to dimeric cations (e.g., $E = 9.6$ and 9.5 for monomeric and dimeric styryl cation, respectively).[5] Therefore, the *E* parameters in Figure 3 can be used to evaluate polymeric carbocation reactivities. The magnitude of the monomer/cation reactivities is quite different, as indicated by the slope of the linear $N-E$ correlation of -0.45. For example, according to the N parameters, the reactivity of αMeSt monomer is ~40 times higher than that of St, whereas according to the E parameters, the reactivity of $\mathrm{P\alpha MeSt}^+$ is >5000 times lower than that of PSt^+. These results are in agreement with previous conclusions that the effect of substituents on carbocation reactivity is much larger than their effect on monomer reactivity.

Conclusions

The $k_p = (5.2 \text{ and } 7.7) \times 10^7$ L mol^{-1} s^{-1} in DCM and DCM/MeCHx 1:1 (v/v), respectively, could be determined by the combination of reaction clock methods. These values are higher than that reported before,[2] but they are in good agreement with the $k_p = 1.2 \times 10^8$ L mol^{-1} s^{-1} value calculated from the E parameter of the cumyl cation and the N parameter of αMeSt using the linear free-energy relationship in a parallel study by Ammer and Mayr.[21] Knowing the true value of k_p for αMeSt allowed us to extend the structure−reactivity scales in cationic polymerization. Consistent with previous conclusions, the current results confirm that the effect of substituents on carbocation reactivity is much larger than their effect on monomer reactivity.

Acknowledgment. Financial support by the National Science Foundation (CHE-0548466) is gratefully acknowledged. P.D. thanks Johannes Ammer and Herbert Mayr for fruitful discussions.

Supporting Information Available: Tables with detailed competition data and ^{1}H NMR spectra of competition products. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Worsfold, D. J.; Bywater, S. *J. Am. Chem. Soc.* **1957**, *79*, 4917–4920.

(2) (a) Williams, F.; Hayashi, K.; Ueno, K.; Okamura, S. *Trans. Faraday Soc.* **1967**, *63*, 1501–1511. (b) Chawla, A. S.; Huang, R. Y. *J. Polym. Sci., Part A: Polym. Chem.* **1975**, *13*, 1271–1284. (c) Villesange, M; Sauvet, G.; Vairon, J. P.; Sigwalt, P. *J. Macromol. Sci.* **1977**, *A11*, 391–410.

(3) Sigwalt, P.; Moreau, M. *Prog. Polym. Sci.* **2006**, *31*, 44–120.

(4) Sipos, L.; De, P.; Faust, R. *Macromolecules* **2003**, *36*, 8282–8290.

(5) De, P.; Faust, R.; Schimmel, H.; Ofial, A. R.; Mayr, H. *Macromolecules* **2004**, *37*, 4422–4433.

(6) De, P.; Faust, R. *Macromolecules* **2004**, *37*, 7930–7937.

(7) De, P.; Sipos, L.; Faust, R.; Moreau, M.; Charleux, B.; Vairon, J.-P. *Macromolecules* **2005**, *38*, 41–46.

(8) De, P.; Faust, R. *Macromolecules* **2004**, *37*, 9290–9294.

(9) De, P.; Faust, R. *Macromolecules* **2005**, *38*, 5498–5505.

(10) Roth, M.; Mayr, H. *Macromolecules* **1996**, *29*, 6104–6109.

(11) Kolishetti, N.; Faust, R. *Macromolecules* **2008**, *41*, 3842–3851.

(12) Kolishetti, N.; Faust, R. *Macromolecules* **2008**, *41*, 9025–9029.

(13) Fodor, Z.; Faust, R. *J. Macromol. Sci.* **1998**, *35*, 375–394.

(14) Nonaka, H.; Ouchi, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 2083–2088.

(15) Weaker nucleophiles such as allylchorodimethylsilane (ACDMS) were used for capping of cumyl cations, followed by UV−vis spectroscopy, but $k^{\pm}{}_p/k_c$ values were impossible to be derived from competition polymerization with αMeSt because of the extremely low reactivity of ACDMS.

(16) De, P.; Faust, R. *Macromolecules* **2006**, *39*, 6861–6870.

(17) Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 7710–7716.

(18) *Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: New York, 1995; Vol. *76*.

(19) (a) Higashimura, T.; Kamigaito, M.; Kato, M.; Hasebe, T.; Sawamoto, M. *Macromolecules* **1993**, *26*, 2670–2673. (b) Li, D.; Hadjikyriacou, S.; Faust, R. *Macromolecules* **1996**, *29*, 6061–6067.

(20) (a) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500–9512. (b) Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66–77. (c) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed.* **1994**, *106*, 990–1010. (d) Schimmel, H.; Ofial, A. R.; Mayr, H. *Macromolecules* **2002**, *35*, 5454–5458. (e) Mayr, H. In *Ionic Polymerizations and Related Processes*; Puskas, J. E., Michel, A., Barghi, S., Paulo, C., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1999; pp 99−115. (f) Patz, M.; Mayr, H.; Bartl, J.; Steenken, S. *Angew. Chem.* **1995**, *107*, 519–521. (g) Roth, M.; Mayr, H. *Angew. Chem.* **1995**, *34*, 2250–2252.

(21) Ammer, J.; Mayr, H. *Macromolecules* **2010**, DOI: 10.1021/ma9024569.