Can Propagation Reaction in Carbocationic Polymerization and Copolymerization of Styrene be Diffusion Controlled ?

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Summary: The reactivity ratios r_1 and r_2 in copolymerizations of styrene and *para*substituted styrenes, for which $r_1 = 1/r_2$, are in contradiction with diffusion control for their propagation reactions. The cross propagation rate constants $k_{12copol}$ in copolymerization of styrene with *p*-chlorostyrene, *p*-methylstyrene and *p*-methoxystyrene have been shown to increase with their nucleophilicity parameter N. This is also not compatible with diffusion controlled cross propagation and propagation, but agrees with similar rate constants of propagation for these monomers. The capping rate constants k_{12capp} of reactions of poly(*p*-methylstyrene)$^{\pm}$ and poly(*p*-methoxystyrene)$^{\pm}$ with π-nucleophiles also increase with N, but with a much larger selectivity. This shows that $k_{12copol}$ and k_{12capp} are not identical. The $k_p^{\pm}$, from 10^9 to $6\ 10^9$ L mol^{-1} s^{-1}, obtained with *p*-chlorostyrene, styrene and *p*-methylstyrene by the Diffusion Clock (DC) method are not consistent with those derived from the ionic species concentration (ISC method) for indene, 2,4,6-trimethylstyrene and *p*-methoxystyrene of the order of 10^4 – 10^5 L mol^{-1} s^{-1}, also measured for living polymerization. These last values are in agreement with those measured previously in nonliving systems, and with an approximate compensation between the reactivity of a monomer and that of the corresponding carbocation.

Keywords: carbocationic copolymerization; diffusion control; electrophilicity; nucleophilicity; propagation rate constant

Introduction

There has been a controversy[1–5] during the last ten years about the values of the propagation rate constants k_p for carbocationic polymerizations of ethylenic monomers with similar initiators and solvents. For styrene and *para*-substituted styrenes in alkylchloride solutions, the difference could be by a factor 10^4 to 10^5 between those deduced from the ionic species concentration (ISC) and values deduced from the competition between propagation and deactivation reactions by strong nucleophiles. The latter were obtained with the assumption that deactivation is diffusion controlled with a rate constant $k_c = k_{diff} = 3\ 10^9$ L mol^{-1} s^{-1} (e.g. in CH_3Cl-methylcyclohexane (MeCHx) 40/60; v/v at −80 °C)[6] leading for example to $k_p^{\pm}$ on ion pairs for styrene and *p*-chlorostyrene of 3–6 10^9 L mol^{-1} s^{-1}.

The large discrepancies between the k_p deduced from an evaluation of the active species concentration (ISC method) of the order of 10^4 to 10^5 L mol^{-1} s^{-1} and those deduced from diffusion controlled deactivation (diffusion clock or DC method) have been discussed in a lecture given at the 14th ACS Ionic Polymerization meeting in 2001 and published later.[4]

Typical results shown at that time were e.g. for styrene $k_p^{\pm} = 2\ 10^4$ L mol^{-1} s^{-1} in CH_2Cl_2 at −80 °C with $HClO_4$ as initiator[7] and $k_p^{\pm} = 5\ 10^9$ L mol^{-1} s^{-1} in CH_2Cl_2/CH_3Cl at −75 °C.[8] For isobutylene (IB) in CH_2Cl_2 k_p is

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equal to 1.2 10^4 L mol^{-1} s^{-1} with Cl_2-Al(ethyl)$_2$Cl at $-45\,°C$[9] and 6 10^8 with 2-chloro-2,4,4-trimethylpentane (TMPCl) and $TiCl_4$ (or $AlCl_3$) at $-78\,°C$ in CH_2Cl_2.[10]

In the present paper, we are planning to show that for *p*-methylstyrene (*p*MeSt), styrene (St) and *p*-chlorostyrene (*p*ClSt) diffusion controlled propagation reactions are incompatible with the reactivity ratios measured for the copolymerization between these monomers and with *p*-methoxystyrene (*p*MeOSt). We will show also that a $k_p^{\pm} \approx 10^9$ L mol^{-1} s^{-1} (and an equilibrium constant of ionization $K_i = 9\ 10^{-8}$ L mol^{-1}) measured by the DC method for *p*MeSt[11] is incompatible with a $k_p^{\pm} = 3\ 10^4$ (and $K_i = 5\ 10^{-4}$ L mol^{-1}) obtained with 2,4,6-trimethylstyrene (TMeSt)[12] in the same solvent at $-30\,°C$.

Methods of Determination of the Propagation Rate Constants

The k_p values, which will be discussed in the present paper have been obtained for living polymerizations in presence of Lewis bases (typically 2,6-di-*tertio*butyl pyridine, D*t*BP). This addition suppresses the formation of unpaired ions (through the effect of a common ion LAX$^-$, see Scheme 1) and gives $k_p^{\pm}$ on ion pairs. They are formed in the equilibrium reaction (with an equilibrium constant K_i) between a halide end group and a Lewis acid (LA).

What is measured is the rate R_p of monomer consumption, which gives the rate constant k_1 for a rate 1st order in monomer concentration.

$$k_1 = k_p \pm K_i[RCl][LA]$$

The concentration of end groups is practically equal to the concentration of the initiator [RCl] and $k_p^{\pm}$ K_i may be calculated.

ISC Method

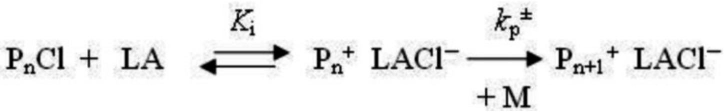
The global k_p obtained in CH_2Cl_2 by the ISC method, based on the total concentration of paired ionic species ($[P^{\pm}]$) and unpaired ionic species ($[P^+]$) with St,[14] 4-isopropyl,α-methyl styrene[17] and *p*MeOSt[15,16] initiated by CF_3SO_3H are given in Table 1. For some monomers, for which K_i has been measured directly on models, the $k_p^{\pm}$ values obtained are not disputed. For polymerizations of indene,[4] TMeSt[12] and *p*MeOSt[13] in the presence of DtBP, $k_p^{\pm}$ values were obtained, which may be compared directly with those measured by the DC method. They are in the range 10^4 to 10^5 between -40 and $-70\,°C$ and similar to those obtained previously in CH_2Cl_2 for non living systems by the ISC method for St[7,14] or *p*MeOSt.[15,16]

Diffusion Clock Method

The other way to obtain $k_p^{\pm}$ is the diffusion clock (DC) method, which does not need the knowledge of the ionic species concentration. It is based on their deactivation by strong nucleophiles with the assumption that it is diffusion controlled, with a rate constant of capping $k_c^{\pm} = k_{diff}$ used as a clock. This method was used before to measure second order rate constants k_{12} of additions of carbocations to ethylenic compounds and applied for the first time by H. Mayr et al. [10] to the determination of k_p of IB in CH_2Cl_2 at $-78\,°C$ ($k_p = 6\ 10^8$ L mol^{-1} s^{-1}). It was extended later by R. Faust et al. to St,[6] *p*MeSt[11] and *p*ClSt[18] with $k_p^{\pm}$ between 10^9 and 4 10^9 L mol^{-1} s^{-1} ($-80 < T < -50\,°C$).

Competition Reaction

Two different DC methods were used. The most frequent has been the competition between reactions of propagation and of



$$P_nCl + LA \underset{}{\overset{K_i}{\rightleftarrows}} P_n^+\ LACl^- \xrightarrow[+M]{k_p^{\pm}} P_{n+1}^+\ LACl^-$$

Scheme 1.

Table 1.
Propagation rate constants k_p obtained in CH_2Cl_2 by the ISC method.

Monomer	Initiator	T °C	k_p L mol^{-1} s^{-1}	Authors
Styrene	ClO_4H CF_3SO_3H	−80 −10	2 10^3 ($k_p^{\pm}$) 2 10^4 (k_p^{+}) 10^5	Pepper[7] Vairon [14]
4-isopropyl, α-methyl styrene	CF_3SO_3H	−40	8 10^3	Vairon [17]
4-methoxystyrene	CF_3SO_3H HMeOStCl/ $SnBr_4$	30	1.3 10^5	Higashimura [15]
		−30	1.8 10^3	Moreau [16]
		−40	8 10^4 ($k_p^{\pm}$)	Faust [13]
2,4,6-trimethylstyrene	CumCl/ BCl_3	−70	1.3 10^4 ($k_p^{\pm}$)	Faust [12]
		−40	2.6 10^4 ($k_p^{\pm}$)	
Indene	CumCl/ $SnCl_4$	−40	10^5 ($k_p^{\pm}$)	Sigwalt [4]

deactivation by a nucleophile (Nu), leading to the capping of the reactive macromolecules ($P^{\pm}$) by Nu. The reaction with methyltriallylsilane (MATMS) gives P-CH_2-$CH(CH_3) = CH_2$, and with 2-phenyl furan (PhFu) or 1,1-ditolylethylene (DTE) gives $PNu^{\pm}$, inactive species for propagation.

The rates of propagation R_p and of capping/termination R_c are respectively

$$Rp = -d[M]/dt = kp^{\pm}\,[P^{\pm}]\,[M]$$

$$R_c = -d[Nu]/dt = kc^{\pm}[P^{\pm}][Nu]$$

Monomer conversion is incomplete and equal to x_∞, and the ratio

$$kp^{\pm}/kc^{\pm} = \frac{Ln(1 - x_\infty)}{Ln(1\text{-}[PCl])/[Nu])}$$

[PCl] being the concentration of the polymer end groups, equal to the initiator concentration [RCl]. With the assumption that $k_c^{\pm} = k_{diff} = 3\ 10^9$ L mol^{-1} s^{-1} in the solvent used (CH_3Cl/ MeCHx; 40/60; v/v) at −80 °C, $k_p^{\pm}$ for St was 1.3 10^9 L mol^{-1} s^{-1} with PhFu and 3.6 10^9 L mol^{-1} s^{-1} with DTE.[6] These values are directly proportional to the assumed k_{diff}, and were in fact equal to k_{diff}.

Capping Reaction

A preformed living polymer $P^{\pm}$ is deactivated by variable concentrations of similar nucleophiles giving inactive carbocations, the concentration of which may be followed from the UV spectra. This gives the rate of capping

$$Rc = kc^{\pm}Ki[P^{\pm}][Nu]$$
$$= kc^{\pm}Ki[PCl][LA][Nu]$$

and then $k_c^{\pm}K_i$. Alternatively $1/R_c$ is plotted against 1/[Nu] and the linear variation observed gives $1/k_i$ as the ordinate to the origin (k_i being the ionization rate constant) and 1/ $k_c^{\pm}K_i$ as the slope.

Assuming $k_c^{\pm} = k_{diff}$, K_i may be calculated and used to obtain $k_p^{\pm}$ from k_1. The values are similar to those obtained in the competition reactions. However $k_p^{\pm}$ is again proportional to k_{diff} since K_i is inversely proportional to $k_c^{\pm} = k_{diff}$.

The $k_p^{\pm}$ obtained by the DC method are given in the Table 2. They do not vary significantly with the coinitiator and with the solvent, and increase very slightly between −50 and −80 °C, which is attributed by the authors to the decrease in solvent polarity. They conclude that these propagation reactions have no enthalpic barrier ($E_p = 0$),[2,6] but the $k_p^{\pm}$ are derived from the nearly equal ratios $k_p^{\pm}$/ $k_c^{\pm}$ when temperature varies. If the relative reactivities of monomer M and nucleophile Nu are independent of the carbocations reactivities (see later) they do not change with temperature and $k_p^{\pm}$/ $k_c^{\pm}$ should remain constant.

Two explanations of the differences between the $k_p^{\pm}$ and K_i values obtained by the ISC and DC methods have been proposed. According to Faust et al.,[34]

Table 2.
Propagation rate constants $k_p^{\pm}$ on ion pairs obtained by the Diffusion Clock method.

Monomer	Solvent	Coinitiator	T	$k_p^{\pm}$ *competition*	$k_p^{\pm}$ *capping*	Ref
			°C	L mol^{-1} s^{-1}	L mol^{-1} s^{-1}	
4-Methylstyrene	CH_2Cl_2	$SnCl_4$	−30	10^9	6.8 10^8	[11]
			−50	1.2 10^9		
			−70	9.7 10^8		
Styrene	CH_2Cl_2	$SnCl_4$	−15	8.4 10^9		[6]
	CH_3Cl/MeCHx (40/60)	$TiCl_4$	−50	1.7 10^9	1.7 10^9	
			−80	1.3 10^9	1.6 10^9	
4-Chlorostyrene	CH_3Cl/MeCHx (40/60)	$TiCl_4$	−80	3 10^9	2 10^9	[18]

the large values result from the much larger electrophilicities of the carbocations poly(St)$^+$, poly(*p*MeSt)$^+$ and poly(*p*ClSt)$^+$ compared to those of poly(TMeSt)$^+$, poly(*p*MeOSt)$^+$ and poly(indene)$^+$.

In our opinion,[4,5] they are resulting from the different method of calculation. For St, *p*MeSt and *p*ClSt propagation reactions, they were obtained on the assumption that the reaction with the nucleophile was diffusion controlled, with a rate constant of capping $k_c^{\pm} \sim 3\ 10^9$ L mol^{-1} s^{-1}. But if $k_c^{\pm}$ is 10^4 times smaller, $k_p^{\pm}$ will be 10^4 times smaller (and K_i 10^4 times larger).

Reactivities of Monomers and Carbocationic Active Species

Propagation rate constants $k_p^{\pm}$ and cross propagation rate constants $k^{\pm}_{12\mathrm{copol}}$ (in copolymerization) are determined by the nucleophilicity of the monomer and by the electrophilicity of the carbocation. In carbocationic homopolymerization of substituted styrenes, a more electron withdrawing substituent of the phenyl ring should decrease the nucleophilicity of the monomer but also increase the electrophilicity of the carbocation.

For polymerizations in bulk by ionizing radiation, which occur on unpaired carbocations, a perfect compensation of these two effects has been suggested[5] to explain the nearly equal rate constants (3-4 10^6 L mol^{-1} s^{-1}) observed for monomers (and their carbocations) having very different nucleophilicities and electrophilicities (see Table 3 and a full discussion in reference[5] pp 89-91). These k_p^{+} were obtained from the measurement of the concentration of the active cations.

Such compensation may also explain the very similar k_p values (10^4 to 10^5) measured for solution polymerization (in CH_2Cl_2) of a variety of monomers, also deduced from an evaluation of the active species concentration. They are similar both for polymerizations initiated by triflic acid (for St, 4-isopropyl,α-methylstyrene and *p*MeOSt) and for living polymerizations of indene, TMeSt and *p*MeOSt (see Table 1).

The rate constant k_{12} of the reaction between an electrophile (1) and a nucleophile (2) has been shown by Mayr et al.[24,25] to be related to an electrophilicity parameter E and to nucleophilicity parameters N and s_N by the relation $\log k_{12} = s_N\,(N + E)$ (at 20 °C). These parameters for (1) and (2) have been found constant for a variety of bimolecular polar reactions, and particularly for those of carbocations with ethylenic compounds (π-nucleophiles).

The N and E parameters are based on rate constants k_{12} of deactivation of e.g. a carbocation C^+ by a nucleophile (Nu). The reference C^+ chosen were benzhydryl carbocations $(RPh)_2CH^+$, BCl_4^-. The E parameter of $(CH_3OPh)_2CH^+$ has been

Table 3.
Propagation rate constants k_p^{+} obtained in bulk in γ-rays initiated polymerization.

Monomer	T	k_p^{+}	Authors
	°C	L mol^{-1} s^{-1}	
Styrene	15	3.5 10^6	Williams, Hayashi [19]
α-Methylstyrene	0	4.3 10^6	Williams, Hayashi [19]
	20	10^6	Huang [20]
4-Methoxystyrene	0	3 10^6	Stannett [21]
Isopropylvinylether	30	1.3 10^6	Stannett [22]

set as a standard with $E = 0$, and the slope s_N of log k_{12} variation with E set to one for a standard monomer, 2-methyl,1-pentene.

The relationship has been verified for a large number of reactions of electrophiles with nucleophiles, and s_N has been found near to 1 (as for 2-methyl,1-pentene) for most π-nucleophiles but near 0.6 for n-nucleophiles and larger than one for arenes (1.6 for xylene).

For the variation of log $k_{12}/\ s_N$ with N of a series of alkenes, reacting with a benzhydryl carbocation, the electrophile specific slope s_E is also near to one.

These two inverse variations of log k with E of the cation and N of the nucleophile are also in favour of an exact compensation of the effects of a substituent on the reactivities of the monomer and of the carbocation.

Relative Reactivities of *p*-substituted Styrenes in Copolymerization

For two monomers M_1 and M_2, the relative reactivities of the monomers can be deduced from the reactivity ratios $r_1 = k_{11}/\ k_{12}$ and $r_2 = k_{22}/\ k_{21}$ of the propagation and cross propagation rate constants. They are often independent of the carbocations M_1^+ or M_2^+ with which they react, which means that $r_1 = 1/r_2$ ($k_{11}/\ k_{12} = k_{21}/\ k_{22}$) or $r_1\ r_2 \sim 1$.

The results obtained by five different research groups for *p*MeSt, St and *p*ClSt, which have been the most studied, show that r_1r_2 is very near to one using various initiators and solvents (Table 4).

The only exceptions (not presented in this table) were observed for radiation initiated copolymerization of *p*ClSt with St or *p*MeSt in nonpolar solvents (benzene or MeCHx), but not in CH_2Cl_2 ($r_1\ r_2 \sim 1$). This was explained by an intramolecular complexation of the more nucleophilic carbocation $p\text{ClSt}^+$ with the penultimate aromatic ring, absent in CH_2Cl_2 acting as a competitive solvating agent.[33]

The mean values of r_1 and $1/r_2$ for the three couples of these monomers (*p*MeST/St, St/*p*ClSt and *p*MeSt/*p*ClSt) in Table 4 have been calculated and show that *p*MeSt is 2.5 times more reactive than styrene, styrene about 2.5 times more reactive than *p*ClSt and *p*MeSt about 6.5 times more reactive than *p*ClSt.

In order to compare the relative reactivity of two carbocations towards the same monomer (e.g. *p*MeSt), one may write $k_{\text{St-}p\text{MeSt}} = 2.5\,k_{\text{St-St}}$ $k_{p\text{ClSt-}p\text{MeSt}} = 6.5\,k_{p\text{ClSt-}p\text{ClSt}}$

So that

$$k_{\text{pClSt-}p\text{MeSt}}/k_{\text{St-}p\text{MeSt}}$$

$$\approx 2.5\,k_{\text{pClSt-pClSt}}/k_{\text{St-St}}$$

which means that $\text{poly}(p\text{ClSt})^+$ is about 2.5 times more reactive than poly(St)^+, if

Table 4.
Relative reactivities of styrenes in carbocationic copolymerization

Comonomers	Acid	Solvent	T °C	r_1	r_2	r_1r_2	Ref.
*p*MeSt/St	$TiCl_4$	CH_2Cl_2	25	3.15	0.36	1.14	[26a]
	WCl_6	Benzene	30	2.48	0.57	1.41	[27]
	$AcClO_4$	CH_2Cl_2	0	2.20	0.44	0.97	[28]
	$AcClO_4$	CH_2Cl_2	0	2.92	0.35	1.02	"
	(+ $n\text{Bu}_4\text{ClO}_4$) $AcClO_4$	CH_2Cl_2/CCl_4	0	3.23	0.36	1.16	"
	Rad.	CH_2Cl_2	−10	2.49	0.41	1.04	[29]
St/*p*ClSt	$SnCl_4$	CCl_4	0	2.5	0.30	0.75	[30]
	WCl_6	Benzene	30	2.08	0.40	0.83	[27]
	$SnCl_4$	$PhNO_2/\ CCl_4$	30	2.1	0.35	0.71	[31]
	$HClO_4$	$C_2H_4Cl_2$	25	2.0	0.43	0.86	[32]
	Rad.	CH_2Cl_2	−10	2.49	0.41	1.03	[29]
*p*MeSt/*p*ClSt	$TiCl_4$	CH_2Cl_2	0	10.5	0.10	1.05	[26b]
	$SnCl_4$	$PhNO_2/\ CCl_4$	30	4.5	0.22	0.99	[31]
	Rad.	CH_2Cl_2	−10	6.64	0.155	1.03	[29]

$k_{p(pClSt)} = k_{p(St)}$ as expected from an exactly inverse relationship between monomer and cation reactivities. This relationship is not proven, but is in agreement with the experimental reactivity ratios and with the low k_p values obtained by the ISC method.

On the opposite, if $k_{St\text{-}St}$ and $k_{pClSt\text{-}pClSt}$ were both diffusion controlled we would have

$$\begin{aligned} k_{St\text{-}pMeSt} &= 2.5 k_{St\text{-}St} \\ &= 2.5 k_{diff} \text{ and } k_{pClSt\text{-}pMeSt} \\ &= 6.5\, k_{pClSt\text{-}pClSt} = 6.5\, k_{diff} \end{aligned}$$

which is meaningless.

Reactivity Ratios in Copolymerization and Nucleophilicities of Monomers

There are fewer copolymerization data for which the much more reactive *p*MeOSt has been compared with *p*MeSt, St and *p*ClSt. In this case, when Hammett plots of $1/r_1$ versus σ of the *p*-substituent were drawn, *p*MeOSt was above the linear variation for the other monomer.[31] But we have found that the original data could also be linearized when $1/r_1$ is plotted against σ+ or the nucleophilicity parameter N of the monomers.

Copolymerizations of *p*MeSt, *p*ClSt and *p*MeOSt with St in benzene[27] (with WCl_6 as coinitiator) permit to measure their relative reactivity toward the poly(St)$^{\pm}$ carbocation. The variation of log $1/r_{1St} =$ log $(k_{12}\ /k_{11})$ is linear with $s_E = 0.59$ (Figure 1). However, r_{1St} with *p*MeOSt is very small leading to a large error. A much better agreement and linearity is observed for the variation of log $r_2 =$ log $(k_{22}\ /k_{21})$ for the various monomers with a slope $s_E = 0.50$. The carbocation changes with each monomer but if $r_1 = 1/r_2$, their relative reactivities do not change.

Another series of reactivity ratios has been measured by Overberger et al.[31] for the copolymerization of αMeSt with *p*ClSt, St, *p*MeSt and *p*MeOSt in CCl_4 with $SnCl_4$ as coinitiator. The variation of log $1/r_{1\alpha MeSt}$ gives the relative reactivities of these monomers with the carbocation poly(αMeSt)$^{\pm}$. It is linear with a slope $s_E = 0.53$ (Figure 2).

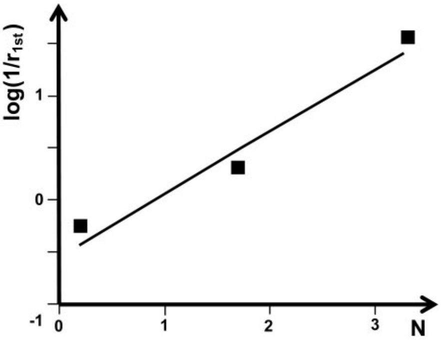


Figure 1.
Relative reactivities in copolymerization of *p*-chlorostyrene, *p*-methylstyrene and *p*-methoxystyrene toward the poly(St)$^{\pm}$ carbocation. Variation of log($1/r_{1copol}$) with the nucleophilicity parameter N of monomers (reference[27]).

When the $\log(1/r_1)$ for polymerizations by radiation are plotted against N, the linearity is much less good, but the slopes s_E are between 0.52 and 0.57 for the reactions of *p*ClSt, St and *p*MeSt with the three carbocations *p*ClSt$^+$, St$^+$ and *p*MeSt$^+$.[29] This shows that the relative reactivities of monomers in copolymerization remain approximately the same for propagation on paired or unpaired ions.

These results with poly(St)$^{\pm}$ and poly(αMeSt)$^{\pm}$ obtained in nonpolar solvents are relative to ion pairs and may be directly

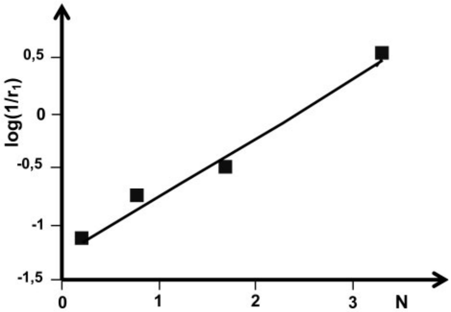


Figure 2.
Relative reactivities in copolymerization of *p*-chlorostyrene, styrene, *p*-methylstyrene and *p*-methoxystyrene toward the poly(α-MeSt)$^{\pm}$ carbocation. Variation of log($1/r_{1copol}$) with the nucleophilicity parameter N of monomers (reference[31]).

compared with the recent data on living polymers.

Relative Reactivities of Monomers in Capping Reactions

Other reactivity ratios have been determined by Faust et al.[34] from the deactivation of *p*MeOSt cation by capping with a series of monomers, and particularly *para*-substituted styrenes.

In the conditions used, ‘‘copolymerization’’ stopped after the addition of one (or a few) units of the comonomer. Similarly to the capping reactions with PhFu or DTE, already described, the polymer yield or its molar masses (Mn) permit to obtain $k_p^\pm / k_c^\pm$. The $k_c^\pm$ values (k_{12capp}) could be calculated from $k_p^\pm$ and they are correct since they are based on $k_p^\pm$ for *p*MeOSt obtained from a spectrophotometric evaluation of $P^\pm$ concentration (see Table 5). But the other values of k_{12capp} given for the other carbocations (poly(*p*MeSt)$^\pm$, poly(St)$^\pm$ and poly(*p*ClSt)$^\pm$) are in our opinion wrong because they are based on the assumption of diffusion controlled propagation for these monomers. These values led for example to the conclusion that the poly(*p*MeOSt)$^\pm$ cation is about 2 10^7 times less reactive than the poly(St)$^\pm$ cation and 10^6 times less reactive than the poly(*p*MeSt)$^\pm$ cation.[34]

But taking into account the monomers reactivities, we have calculated that if the rate constant of e.g. *p*MeSt is 10^5 L mol^{-1} s^{-1}, as we have suggested, poly(*p*MeSt)$^\pm$ is only about 50 times more reactive than poly(*p*MeOSt)$^\pm$, in agreement with a reactivity of *p*MeOSt in capping reactions about 50 times that of *p*MeSt, as found by Faust et al. This would be in agreement with a perfectly inverse relationship between monomer nucleophilicity and carbocation electrophilicity.

The reactivity ratios $r_{1capp} = k_{11} / k_{12capp}$ obtained in these experiments have been assumed to be identical with $k_{11} / k_{12copol}$ obtained in copolymerizations. But when the variation of log $(1/r_{1capp})$ proportional to k_{12capp} is plotted against the nucleophilicity parameter N of a series of monomers, the electrophile specific slope s_E is near one (Figure 3; $s_E = 0.93$).

This was to be expected since the N parameters have been deduced from rate constants k_{12} for the standard deactivation reactions of benzhydryl carbocations with a π-nucleophile, for which $s_E \sim 1$.

This capping study of poly(*p*MeOSt)$^\pm$ has been extended in a recent paper of R. Faust et al.[36] to that of poly(*p*MeSt)$^\pm$ by a series of monomers M2 giving poly(*p*MeSt)$_n$M2Cl. The $k_p^\pm / k_c^\pm$ values obtained permit the calculation of $k_c^\pm = k_{12capp}$, assuming that $k_p^\pm = k_{11}$ for *p*MeSt is equal to 10^9 L mol^{-1} s^{-1} in CH_2Cl_2, which we do not accept, contrarily to k_{12capp} values for poly(*p*MeOSt)$^\pm$, based on $k_p^\pm$ for *p*MeOSt obtained by the ISC method. But even if the absolute values of k_{12capp} on poly(*p*MeSt)$^\pm$ are wrong by the same factor, their variation with the nucleophilicities of the monomers are significant. In the solvent CH_2Cl_2/MeCHx (50/50; v/v) at −40 °C they decrease from k_{diff} for *p*MeOSt to 3 10^8 L mol^{-1} s^{-1} (*p*MeSt), 6.2 10^7 (St), 4.2 10^7 (*p*ClSt) and 3 10^6 L mol^{-1} s^{-1} for butadiene.[36] The variation of log k_{12capp} with N of the monomers has a slope $s_E = 0.72$. This may

Table 5.
Rate constants of capping k_{12capp} for polymeric carbocation reactions with styrenes in CH_2Cl_2/ MeCHx (50/50) at −40 °C.[34]

Monomer	k_{12capp}				k_{22} / k_{12capp}
	L mol^{-1} s^{-1}				
	poly(*p*MeOSt)$^\pm$	poly(*p*MeSt)$^\pm$	poly(St)$^\pm$	poly(*p*ClSt)$^\pm$	
p-Methoxystyrene	7800	*Diff. ltd*	*Diff. ltd*	*Diff. ltd*	1
p-Methylstyrene	186	2 10^8	*Diff. ltd*	*Diff. ltd*	10^6
Styrene	26		4 10^9	*Diff. ltd*	1.5 10^8
p-Chlorostyrene	10			3 10^9	3 10^8

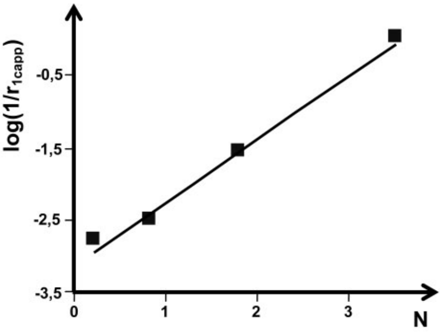


Figure 3.
Relative reactivities in capping reaction of poly(*p*-methoxystyrene)$^{\pm}$ by *p*-chlorostyrene, styrene, *p*-methylstyrene and *p*-methoxystyrene. Variation of log($1/r_{1capp}$) with the nucleophilicity parameter N of monomers (reference[34]).

indicate a decrease in the selectivity of the more reactive carbocation poly(*p*MeSt)$^{\pm}$ compared to poly(*p*MeOSt)$^{\pm}$. But s_E is still much larger than that observed for $k_{12copol}$ in copolymerization reactions.

Relative Reactivities of Carbocations in Copolymerization and in Capping Reactions

If the propagation reaction of poly(St)$^{\pm}$ with St ($N = 0.78$) is already diffusion controlled ($k_{st\text{-}st} = k_{diff}$) the cross propagation constant k_{12} with *p*MeSt ($N = 1.7$) and *p*MeOSt ($N = 3.1$) should not have increased regularly with N. With the less reactive poly(α-MeSt)$^{\pm}$, diffusion control is still less likely, while the variation of log k_{12} is nearly the same.

The slopes s_E observed in copolymerizations of *p*ClSt, St, *p*MeSt and *p*MeOSt (0.50 to 0.59) reflect the smaller selectivity of a growing carbocation toward the monomer than in capping, and may correspond to a larger intrinsic barrier than in capping experiments. This could be in agreement with rates of homopolymerization and copolymerization lower than expected from the electrophilicity parameters measured in capping reactions.

However, there is still a question about the validity of the E parameters larger than 6 derived from capping reactions. A reactivity of poly(*p*MeSt)$^{\pm}$ larger by a factor 10^6 than that of poly(*p*MeOSt)$^{\pm}$ appears too large to be credible. And even if diffusion control occurred in poly(*p*MeSt)$^{\pm}$ capping (which may be disputed), since $E = 4.7$ for poly(*p*MeOSt)$^{\pm}$ and $6.5 < E < 7$[37] for poly(*p*MeSt)$^{\pm}$, a $\Delta E \sim 2$ between the two carbocations should lead to poly(*p*MeSt)$^{\pm}$ only about 10^2 times more reactive.

What may be the explanation of the much lower values of the electrophile specific slope $s_E \sim 0.55$ observed in copolymerizations involving e.g. poly(αMeSt)$^{\pm}$ and *p*ClSt, St, *p*MeSt or *p*MeOSt, instead of $s_E = 0.93$ for the capping of poly(*p*MeOSt)$^{\pm}$?

This may indicate that the types of reaction are different, one being a simple deactivation and the other a propagation step, which includes deactivation with incorporation of a monomer unit and formation of a new carbocation. The time of incorporation may be increased by a resonance stabilization of a transitory complex, which may be still larger in the case of styrenes, for which the carbocation bears an aromatic substituent. This was suggested in our former publications,[4,5] in which we proposed that capping and propagation are two-step reactions with a preliminary complexation equilibrium of $P^{\pm}$ with the monomer M or the nucleophile Nu (with equilibrium constants K_{Nu} and K_M) (*see* ref.[5] § 7.1 pp 102-105).

Another reason, which should be considered for the small $k_p^{\pm}$ for propagation reactions of styrenes is a deactivation of the growing carbocations by the penultimate unit aromatic ring. Such an effect may explain the large difference by a factor 10^4 between the rates of the monomer addition on the first unit HSt^+, or on the second $HStSt^+$ and following units $H(St)_n^+$, observed in laser flash photolysis of St and substituted styrene monomers(see discussion in ref[5] pp 94-95). This effect may also occur, even if it is attenuated, for propagation involving ion pairs.

Direct Comparison of $k_p^{\pm}$ of Styrene and Substituted Styrenes

The results obtained with the DC method for *p*ClSt, St and *p*MeSt are given on

Table 2. There is a good agreement between the $k_p^{\pm}$ obtained through the competition or the capping reactions, and between those measured with either $SnCl_4$ or $TiCl_4$ as coinitiators. Most of the $k_p^{\pm}$ are in the range 10^9 to 3 10^9 L mol^{-1} s^{-1}, i.e. with propagation diffusion controlled or very near to it.

But if we look at the results obtained (also for living polymerizations in CH_2Cl_2) with indene, TMeSt and *p*MeOSt, the $k_p^{\pm}$ are 10^4 times smaller because they have been in this case deduced from the cationic species concentration, calculated from the K_i measured by spectrophotometry of the model monomeric carbocations (Table 6).

The comparison between *p*MeSt and TMeSt in CH_2Cl_2 is particularly striking. *p*MeSt is about 6 to 8 times more reactive than TMeSt, and the difference between the $k_p^{\pm}$ by a factor 10^4 has been attributed by Faust to the much larger reactivity of the carbocation *p*MeSt$^+$ and /or possibly to a steric effect in the addition of TMeSt to poly(TMeSt)$^+$. But in copolymerization of TMeSt with St,[38] its addition on poly- (TMeSt)$^+$ is slower than styrene addition by a factor of 2.70 ± 0.05, while its addition on poly(St)$^+$ is slower by a factor of 1.8 ± 0.2, showing no significant difference between propagation for TMeSt and cross propagation with styrene.

The reactivity of TMeSt in copolymerizations is lower than that of styrene, contrary to expectations. This has been explained by Maréchal[39] by the presence of two methyl groups in ortho position, which strain the vinyl groups out of the plane of the phenyl group, preventing their conjugation, as was confirmed by ^{1}H NMR. A similar inhibition of conjugation should also increase the reactivity of the carbocation. This is confirmed by the electrophilicity parameter of poly-(TMeSt)$^+$: $E = 6.16$.[40] Since E for *p*MeSt may be evaluated to be between 6.5 and 7,[37] the carbocation reactivity should differ by less than a factor of ten.

Even if the E/N scale could be used for the calculation of $k_p^{\pm}$ - which is disputable - the difference in $k_p^{\pm}$ should have been only by a factor of about 50.

There is also a large discrepancy between the rate constants of recombination of ion pairs k_{-i} (see Table 6), obtained either from K_i and k_i or from rapid monomer consumption involving the initiation step (RMC data).[5] The k_{-i} for poly(TMeSt)$^+$ is 5.8 10^3 s^{-1} at $-30\,^{\circ}$C, of the same order of magnitude as those of a variety of ion pairs (*see* in Table 6, ref[5] p 67), while $k_{-i} = 1.2$ 10^7 at $-30\,^{\circ}$C for poly(*p*MeSt)$^{\pm}$ by the DC method. This is not expected from a ΔE of about 0.5 between these two carbocations.

For *p*MeOSt polymerization, the $K_i = 9$ 10^{-3} L mol^{-1} with $SnBr_4$ is what could be expected by comparison to TMeSt, and $k_p^{\pm}$ is equal to 1.1 10^5 L mol^{-1} s^{-1}. This value is similar to those measured in CH_2Cl_2 for indene at $-40\,^{\circ}$C ($k_p^{\pm} = 10^5$; $K_i = 1.510^{-2}$ L mol^{-1}).[4]

It has been shown by JP Kennedy et al.[41] that the rates of living copolymerization of *p*MeSt and indene are independent of the molar amounts of these monomers between 12 and 70% of indene. We have concluded[5] that this is possible only if their rates of cross propagation and propagation are similar, i.e. of the order

Table 6.
Rate Constant $k_p^{\pm}$, ionization equilibrium constant K_i, enthalpic changes ΔH_i and rate constant of ion pair recombination k_{-i} for the propagation reaction of various styrenes in CH_2Cl_2.

Monomer	Acid	T °C	$k_p^{\pm}$ L mol^{-1} s^{-1}	K_i L mol^{-1}	ΔH_i kcal mol^{-1}	k_{-i} kcal mol^{-1}	Method	Ref.
Indene	$SnCl_4$	−40	10^5	1.5 10^{-2}	−4	5.2 10^2	ISC	[4]
*p*MeOSt	$SnBr_4$	−30	1.1 10^5	9.1 10^{-3}	−4.2	–	ISC	[13]
TMeSt	BCl_3	−30	3.5 10^4	5 10^{-4}	−3.5	5.8 10^3	ISC	[12]
*p*MeSt	$SnCl_4$	−30	$\geq$ 6.8 10^8	9.4 10^{-8}	4.3	1.2 10^7	DC	[18]

of 10^4 to 10^5 L mol^{-1} s^{-1}, as for the other monomers when they are based on ionic species concentration.

The conclusion is that the large differences between published $k_p^{\pm}$, $k_{\text{-i}}$ and K_i of *p*MeSt and TMeSt result mainly from the different methods of determination. Since the copolymerization data show that the propagation rate constants $k_p^{\pm}$ for St, *p*ClSt and *p*MeSt cannot be diffusion controlled, the correct values should be those deduced from the ionic species concentration (ISC method). This is also the case for their ionization equilibrium constants K_i. The values of $k_p^{\pm}$ obtained for living polymerizations of TMeSt and *p*MeOSt (10^4 to 10^5 L mol^{-1} s^{-1}) are also in agreement with a nearly exact compensation between the nucleophilicity of the monomer and the electrophilicity of the corresponding carbocation. Such a compensation is also necessary in order to explain why $r_1 \sim 1/r_2$ in copolymerizations between *p*ClSt, styrene, *p*MeSt and *p*MeOSt.

A comparison between TMeSt and St (or *p*ClSt) may seen more difficult since only one set of directly comparable data (see Table 2) is available for St (in CH_2Cl_2 with $SnCl_4$ at $-15\,°C$) [6] giving $k_p^{\pm} = 8\ 10^9$ L mol^{-1} s^{-1} and $K_i = 10^{-11}$ (in L mol^{-1}). But it may be calculated that the $K'_{i\ (TiCl4)} = 10^{-11}$ (in L^2 mol^{-2}) obtained in CH_3Cl/ MeCHx (40/60; v/v) is larger than an apparent $K_{i\ (TiCl4)}$, but only by a factor of about three. While $TiCl_4$ is a much stronger acid than $SnCl_4$, a $K'_{i\ (TiCl4)}$ of about 10^{-7} L^2 mol^{-2} was obtained for St at $-80\,°C$ by the DC method, while the experimental $K_{i\ (SnCl4)} = 2.5\ 10^{-3}$ L mol^{-1} for TMeSt at $-70\,°C$.

These two sets of results (obtained by the same authors) are not compatible and $k_p^{\pm} \sim k_{diff}$ for St appears quite unlikely, in agreement with the data for copolymerization reactions.

Conclusion

In copolymerization with St, the increase of the cross propagation rate constants $k_{12copol}$ between poly(St)$^+$ and *p*ClSt, *p*MeSt and *p*MeOSt, when their nucleophilicity increases, is in contradiction with diffusion controlled cross propagation or propagation for styrene. The values of r_1r_2 near one in copolymerizations of *p*ClSt, St and *p*MeSt are also incompatible with such a diffusion control.

The difference between the rate constants of termination by capping of a carbocation k_{12capp} and the cross propagation rate constants $k_{12copol}$ in copolymerization is reflected by the larger selectivity toward the monomers in the first case.

Copolymerizations reactivity ratios of *p*ClSt, St, *p*MeSt and *p*MeOSt have been shown to be in agreement with a nearly exact inverse relationship between the monomer reactivities and those of the corresponding carbocations. The k_p measured for nonliving systems, of the order 10^4 to 10^5 for styrenes, are in agreement with this relationship and with $k_p^{\pm}$ values obtained for living polymerizations of aromatic monomers (indene, *p*MeOSt, TMeSt) from the ionic species concentration (ISC method).

A direct comparison of the various parameters ($k_p^{\pm}$, K_i and $k_{\text{-i}}$) obtained in the same conditions for the propagation reactions of *p*MeSt (DC method) and TMeSt (ISC method) living polymerizations shows that they are not compatible. But they become compatible if the $k_p^{\pm}$ for *p*MeSt is of the order of 10^5 L mol^{-1} s^{-1}.

In the case of St and *p*ClSt, the DC method has led to values of $k_p^{\pm}$, $k_{\text{-i}}$ and K_i of the same order of magnitude as those of *p*MeSt, which are incompatible with both their copolymerization data and with the kinetic parameters measured for other aromatic monomers by the ISC method. It was shown that the explanation of values near to k_{diff} for *p*MeSt, St and *p*ClSt, linked to a reactivity (and an electrophilicity) of the carbocations larger than that of poly(*p*MeOSt)$^{\pm}$ by factors 10^6 to 10^8, cannot be justified. We conclude that diffusion control does not occur in the propagation reaction of *p*MeSt and is quite unlikely for St and *p*ClSt.

N. B.: The results of two recent papers [43,44] do not disagree with our main conclusions: [5,42]

1) For styrenes, there is compensation between monomer and carbocations reactivities in polymerizations leading to similar k_p.
2) The activation energy for their propagation is not equal to zero.
3) Capping rate constants (with deactivation) are different from propagation rate constants k_p.

Deactivation experiments by H. Mayr et al. [43] of $H\alpha MeSt^+$ (cumyl cation) in CH_2Cl_2 at 20 °C led to an electrophilicity parameter $E = 5.74$, in accordance with previous measurements for $HpMeOSt^+$ (4.7), Ph_2CH^+ (5.9) and $HpMeSt^+$ (~ 6.7). A calculated rate constant $k^1_{\alpha MeSt}$ for its reaction with α–methylstyrene (αMeSt) led to $k^1_{\alpha MeSt} = 2\ 10^8$ L mol^{-1} s^{-1} while $k^1_{pMeOSt} = 10^8$ L mol^{-1} s^{-1} (at 20 °C for both monomers, $E + N \sim 8$).

If $k^1_{\alpha MeSt}$ is equal to $k_{p\alpha MeSt}$, as assumed by Mayr et al., the calculated values at 20 °C might be compatible with the rate constants at low temperature, derived from the concentration of ionic species: $k^1_{\alpha MeSt} = 3\ 10^5$ L mol^{-1} s^{-1} at −65 °C by R. Russell et al.[45] and $k_p^{\pm} = 1.1\ 10^5$ L mol^{-1} s^{-1} at −60 °C for *p*MeOSt by Faust et al.[13] The differences by a factor 10^3 may result from an activation energy E_p of about 6 kcal mol^{-1}, as found for the $k_p^{\pm}$ of *p*MeOSt.[13] It might also result from the difference in reactivities between monomeric and polymeric cations as observed by Mc Clelland, Steenkeen et al.[9,46]

R. Faust et al.[44] have measured for α–methylstyrene a propagation rate constant $k_p^{\pm} = 5.7\ 10^7$ L mol^{-1} s^{-1} at −80 °C from competition reactions with various silanes, with the assumption that the reaction with 1-trimethylsiloxy-cyclopentene ($N = 6.57$) is diffusion controlled. This is in contradiction with the value 3 10^5 L mol^{-1} s^{-1} obtained at −65 °C from the ionic species concentration.[45] The authors concluded that the "agreement" with $k^1_{\alpha MeSt} = 1.1\ 10^8$ L mol^{-1} s^{-1} calculated by Mayr showed that the reaction was temperature independent ($E_p \sim 0$), which is quite unlikely,[42] since E_p of about 6 kcal mol^{-1} for *p*MeOSt propagation was found earlier by the same group.[13]

Our conclusion that the capping and copolymerization reactions are of a different type is confirmed by the capping experiments of $H\alpha MeSt^+$ with the series of styrene monomers *p*ClSt, St, *p*MeSt and *p*MeOSt (see Table 3 in ref 44), for which log k_{12} increases linearly with N with a slope $s_E = 1.53$, much larger than that observed with poly$(\alpha MeSt)^+$ and the same monomers in a copolymerization with αMeSt ($s_E = 0.53$).[42]

In Figure 4 (in ref [44]) when the controversial value $E = 9.5$ for styrene is excluded, the slope of log N versus log E is equal to −0.78 and when styrene monomers only are considered (αMeSt and *p*MeOSt) the slope is then equal to −0.96, in agreement with an inverse relationship between the reactivity of these carbocations and that of the corresponding monomers.

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