Reactivity of Chlorostyrenes in Cationic Polymerization

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ABSTRACT

The reactivity ratios relative to cationic polymerization of three chlorostyrenes and styrene were studied. The values of r_1 and r_2 were determined for various experimental conditions. The influence of the solvent, of the polymerization temperature, of the nature of the initiator and of the molecular weight distribution were examined in particular. The relative activation entropies and enthalpies were determined (against styrene as reference) and an isokinetic relationship was found for 2- and 3-chlorostyrenes. All the experimental reactivities were correlated with the quantum chemistry parameters. From this correlation it is found that the interaction is possible not only with C8, but also with C7 and Cl, depending on the nature of the monomer.

INTRODUCTION

For several years, we have studied the cationic polymerization
and copolymerization of halogenated monomers such as chloro-,
fluoro-, and bromoindenes [1-4] or fluorostyrenes [5]. The values
of reactivity ratios determined for the copolymerization with indene
or with styrene have been analyzed and compared with the stabiliza-
tion energies calculated by quantum chemistry methods. In a few
cases a discrepancy between theoretical and experimental values
has been observed. For example, with the system 6-chloroindene-
styrene the values of r_1 and r_2 were both below 1 [3]. Such a
result was found by Plesch [6] for the system 4-chlorostyrene-
styrene, but with the same system and other experimental conditions
Ikeda, Higashimura, and Okamura [7] found $r_1 < 1$ and $r_2 > 3.6$. In
order to ascertain the influence of experimental conditions on the
copolymerization of chlorostyrenes with styrene and to verify the
existence of a correlation between their reactivity estimated from
reactivity ratios and calculated by quantum chemistry we studied
the polymerization of monofluoro- and monochlorostyrene.

A previous article dealt with monofluorostyrenes [5], and pre-
liminary results on 4-chlorostyrene copolymerization have been
published [8]. Various partial studies of the reactivity of the chloro-
styrenes can be found in the literature (see Table 6) [9-12], but we
did not find any systematic study of the variations of r_1 and r_2 with
regard to the experimental conditions, particularly temperature.

EXPERIMENTAL

The monomers were prepared by dehydration of the corresponding
(chlorophenyl)-1 ethanols; these alcohols were obtained by condensa-
tion of the corresponding chlorobenzaldehydes with methyl-magnesium
iodide. Their characteristics were as follows: 2-chlorostyrene
(2-Cl), bp 26°C/0.2 Torr, n_D^{20} = 1.5640; 3-chlorostyrene (3-Cl), bp
21°C/0.005 Torr, n_D^{20} = 1.5625; 4-chloro (4-Cl), bp 24.5°C/0.01 Torr,
n_D^{24} = 1.5645.

All these monomers are pure by gas chromatography (Chromosorb
SE 30), and their NMR spectra are in good agreement with their
structure.

Methylene chloride was purified according to N'guyen ank Hung
[13] as described in a previous study [5].

Nitrobenzene and the carbon tetrachloride were the commercial products purified by a high reflux ratio distillation. The reactions were run under deoxygenated conditions under dry nitrogen. The reactivity ratios were determined by the intersection and the Kelen-Tüdős methods. The copolymers were analyzed either by infrared spectroscopy or by elementary analysis. The 4-chlorostyrene-styrene and 3-chlorostyrene-styrene copolymers were analyzed by infrared spectroscopy in CS_2 solution, the bands attributed to a poly-4-chlorostyrene (1100 cm^{-1}) and polystyrene (7000 cm^{-1}) being used. The 3-chlorostyrene-styrene copolymer was analyzed by chlorine determination.

A gel-permeation chromatographic study was run on a Water Associates Chromatoprep 100 instrument in benzene at 1% concentration. The columns were packed with crosslinked polystyrene. The detector was a differential refractometer.

RESULTS AND DISCUSSION

As in our previous studies, the electronic characteristics of the monomers and of the relative cations were determined. The stabilization energies $(\Delta E)_r{}^S$ relative to their reactions with various styryl cations have been calculated.

The theoretical study was carried out by both the Pöple and Hückel methods. The results obtained according to Pöple (CNDO II) are reported in Table 1, where S_r is the superdelocalizability on carbon r.

The numbering of the styrene molecule is as shown in structure I.

I
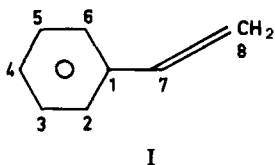
Table 2 reports values of the stabilization energies calculated according to Hückel by use of the following parameters: $\alpha_{Cl} = \alpha + 1.8\beta$; $\beta_{C-Cl} = 0.6\beta$; $\alpha_{adj} = \alpha + 0.3\beta$ (where α_{adj} is α for the carbon adjacent to the chlorine).

The values listed in Tables 1 and 2 will be discussed with the corresponding experimental results.

TABLE 1. Values of the Superdelocalizability S_r on Carbon 8 of the Various Halostyrenes and of Styrene as Calculated by the CNDO II Method

Monomer	S_r on C_8
2-Cl	1.837
3-Cl	1.840
4-Cl	1.831
S	

TABLE 2. Stabilization Energies for the Reaction of Monomers M (Styrene and Monochlorinated styrenes) and Their Corresponding Cations $(M^{\oplus})$

	Stabilization energies			
	$S^{\oplus}$	$2\text{-Cl}^{\oplus}$	$3\text{-Cl}^{\oplus}$	$4\text{-Cl}^{\oplus}$
S	0.807	0.800	0.807	0.815
2-Cl	0.799	0.792	0.799	0.806
3-Cl	0.807	0.800	0.807	0.814
4-Cl	0.799	0.791	0.799	0.806

Nature of the Solvent

Throughout the study CH_2Cl_2 has been used; however in the case of 4-chlorostyrene the influence of the nature of the solvent was examined. The following conditions have been used: $\theta = 5°C$; $[TiCl_4] = 0.01$ mole/liter; $[M] = 0.2$ mole/liter, where $[M]$, $[A]$, and θ are the monomer and initiator concentrations (mole/liter) and the polymerization temperature, respectively. Generally, the subscript 2 refers to styrene and the subscript 1 to the chlorostyrenes. The results are reported in Table 3.

The results reported in Table 3 indicate that, whatever the solvent, styrene is more reactive than the chlorostyrene towards both styryl and 4-styryl cation. This fact is in agreement with the values of stabilization energy calculated for the reaction of these two monomers

TABLE 3. Effect of Solvent on Dielectric Constant D, Dipole Moment μ and Reactivities in the System 4-Chlorostyrene (1)-Styrene (2)[a]

Solvent	D	μ (Debyes)	r_1	r_2	$1/r_2$	$r_1 r_2$
CCl_4	2.2	0	0.24 ± 0.08	3.7 ± 0.7	0.27	0.89
CH_2Cl_2	9.1	1.57	0.51 ± 0.09	3.7 ± 0.2	0.27	1.89
$C_6H_5NO_2$	29.7	4.27	0.43 ± 0.09	1.9 ± 0.2	0.52	0.82

[a] $[TiCl_4]$ = 0.01 mole/liter; $[M]$ = 0.2 mole/liter; θ = 5°C.

either with styryl or 4-styryl cation. The variations of r_1 and r_2 with respect to $1/D$ do not observe a linear relationship as it was the case with 4-fluorostyrene [5], and no direct explanation can be provided. In fact, the values of r_1 and r_2 depend on (a) preferential solvation, (b) association at the carbocation and counterion, and (c) orientation of solvent molecules.

Preferential Solvation

If the solvent has a poor solvating power, the active species is solvated mainly by the most solvating monomer (4-chlorostyrene). When the solvating power of the solvent increases (particularly with nitrobenzene), the active species is solvated by the solvent, and the relative concentrations of the monomers are the same around the active centers and in the solution.

Degree of Association of Carbocation and Counteranion

When the solvent has a very low polarity, the ion pair is closely associated, but as the polarity of the solvent increases, the carbocation and its counter anion become less and less associated. In nitrobenzene, most of the active centers are free ions.

Orientation of Solvent Molecules near the Active Center

Around the active center, the value of D can be very different from its value in solution, because the electric field due to the charged species of the chain end causes orientation the solvent dipoles into preferential directions.

The results reported in Table 3 do not allow one to determine the contribution of each of these parameters.

Temperature of Polymerization

Let k_{ij}, A_{ij}, and $H_{ij}^{\ddagger}$ be the rate constant, the preexponential factor, and the activation enthalpy relative to the reaction of the cation i with the monomer j. According to the Arrhenius law and to the definition of $r_{ij} = k_{ii}/k_{ij}$ we can write:

$$r_{ij} = (A_{ii}/A_{ij})(\exp-\{\Delta H_{ii}^{\ddagger} - \Delta H_{ij}^{\ddagger}\}/RT) \tag{1}$$

or, for $\Delta S^{\ddagger}$ as the activation entropy:

$$r_{ij} = (\exp\{\Delta S_{ii}^{\ddagger} - \Delta S_{ij}^{\ddagger}\}/R)(\exp-\{\Delta H_{ii}^{\ddagger} - \Delta H_{ij}^{\ddagger}\}/RT) \tag{2}$$

According to Eq. (2), the plot of variation of r_{ij} with respect to $1/T$ is a straight line whose slope is $(\Delta H_{ii}^{\ddagger} - \Delta H_{ij}^{\ddagger})/R$ and whose intercept is $\Delta S_{ii}^{\ddagger} - \Delta S_{ij}^{\ddagger}$.

In the study of temperature dependence the solvent was CH_2Cl_2 and the initiator $TiCl_4$, $[TiCl_4] = 0.003$ mole/liter and $[M] = 0.1$ mole/liter.

The results for 2-chloro-, 3-chloro-, and 4-chlorostyrenes are given in Tables 4, 5, and 6, respectively. The corresponding straight lines are reported on Figs. 1, 2, and 3, respectively. From the intercepts and the slopes the values of $\Delta H_{ii}^{\ddagger} - \Delta H_{ij}^{\ddagger}$ and $\Delta S_{ii}^{\ddagger} - \Delta S_{ij}^{\ddagger}$ can be obtained. In the following discussion, in order to discuss simultaneously the three sets of values without any danger of confusion the styrene will be denoted by S and the three chlorined monomers will be denoted respectively by 2Cl, 3Cl, and 4Cl. For example the reactivity ratios for the pair styrene-4-chlorostyrene are $r_{S4Cl} = k_{SS}/k_{S4Cl}$ and $r_{4ClS} = k_{4Cl\ 4Cl}/k_{4ClS}$.

The values thus obtained were:

$$\Delta H_{2Cl-2Cl}^{\ddagger} - \Delta H_{2Cl-S}^{\ddagger} = 0 \text{ kcal/mole}$$

$$\Delta H_{S-S}^{\ddagger} - \Delta H_{S-2Cl}^{\ddagger} = 0.77 \text{ kcal/mole}$$

$$\Delta H_{3Cl-3Cl}^{\ddagger} - \Delta H_{3Cl-S}^{\ddagger} = 0$$

TABLE 4. Effect of Polymerization Temperature on 2-Chlorostyrene (1)-styrene (2) System[a]

$\theta°(C)$	r_1	r_2	$1/r_2$	r_1r_2
25	0.8 ± 0.1	4.3 ± 0.3	0.23	3.4
0	0.66 ± 0.06	4.1 ± 0.1	0.24	2.7
-30	0.66 ± 0.06	3.5 ± 0.1	0.28	2.3
-75	0.71 ± 0.03	2.31 ± 0.07	0.43	1.6

[a] $[TiCl_4]$ = 0.003 mole/liter; $[M]$ = 0.1 mole/liter; solvent CH_2Cl_2.

TABLE 5. Effect of Polymerization Temperature on 3-Chlorostyrene (1)-Styrene (2) System[a]

$\theta°(C)$	r_I	r_2	$1/r_2$	r_1r_2
25	0.37 ± 0.05	3.7 ± 0.1	0.27	1.4
0	0.38 ± 0.04	3.2 ± 0.1	0.31	1.2
-30	0.37 ± 0.03	2.5 ± 0.1	0.40	0.5
-70	0.35 ± 0.06	2.0 ± 0.1	0.50	0.7

[a] $[TiCl_4]$ = 0.003 mole/liter; $[M]$ = 0.1 mole/liter; solvent CH_2Cl_2.

$$\Delta H_{S-S}^{\ddagger} - \Delta H_{S-3Cl}^{\ddagger} = 0.81 \text{ kcal/mole}$$

$$\Delta H_{4Cl-4Cl}^{\ddagger} - \Delta H_{4Cl-S}^{\ddagger} = -0.43 \text{ kcal/mole}$$

$$\Delta H_{S-S}^{\ddagger} - \Delta H_{S-4Cl}^{\ddagger} = 0.19 \text{ kcal/mole}$$

$$\Delta S_{2Cl-2Cl}^{\ddagger} - \Delta S_{2Cl-S}^{\ddagger} = -0.69 \text{ cal/mole-°K}$$

$$\Delta S_{S-S}^{\ddagger} - \Delta S_{S-2Cl}^{\ddagger} = 5.57 \text{ cal/mole-°K}$$

$$\Delta S_{3Cl-3Cl}^{\ddagger} - \Delta S_{3Cl-S}^{\ddagger} = -1.99 \text{ cal/mole-°K}$$

FIG. 1. Variation of log r_1 and log r_2 with $10^3/T$ (°K): (1) 2-chloro-styrene; (2) styrene. [$TiCl_4$] = 0.003 mole/liter; [M] = 0.1 mole/liter; solvent, CH_2Cl_2.

$$\Delta S_{S-S}^{\ddagger} - \Delta S_{S-3Cl}^{\ddagger} = 5.29 \text{ cal/mole-°K}$$

$$\Delta S_{4Cl-4Cl}^{\ddagger} - \Delta S_{4Cl-S}^{\ddagger} = -3.37 \text{ cal/mole-°K}$$

$$\Delta S_{S-S}^{\ddagger} - \Delta S_{S-4Cl}^{\ddagger} = 3.35 \text{ cal/mole-°K}$$
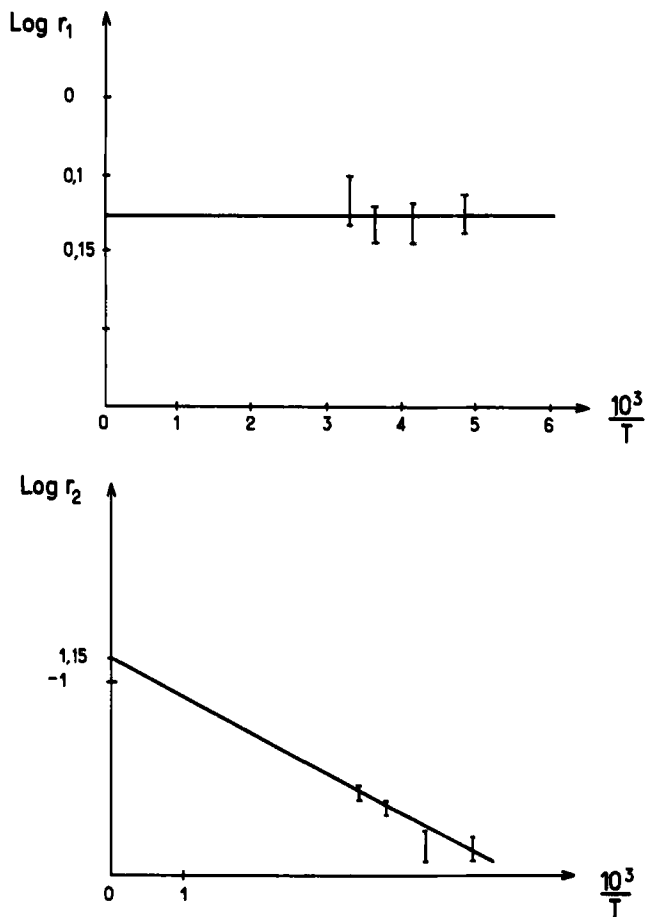
FIG. 2. Variation of log r_1 and log r_2 with $10^3/T$ (°K): (1) 3-chloro-styrene; (2) styrene. [TiCl$_4$] = 0.003 mole/liter; [M] = 0.1 mole/liter; solvent, CH$_2$Cl$_2$.

Figure 4 shows that the two straight lines corresponding to the variations of log r_2 against $10^3/T$ for 2Cl and 3Cl intersect at the same point with the straight line log r_2 = 0. Moreover the straight lines corresponding to the 2-, 3-, and 4-fluorostyrenes [5] intersect at the same point. According to Exner [14], such an intersection is in agreement with the existence of an isokinetic relationship between
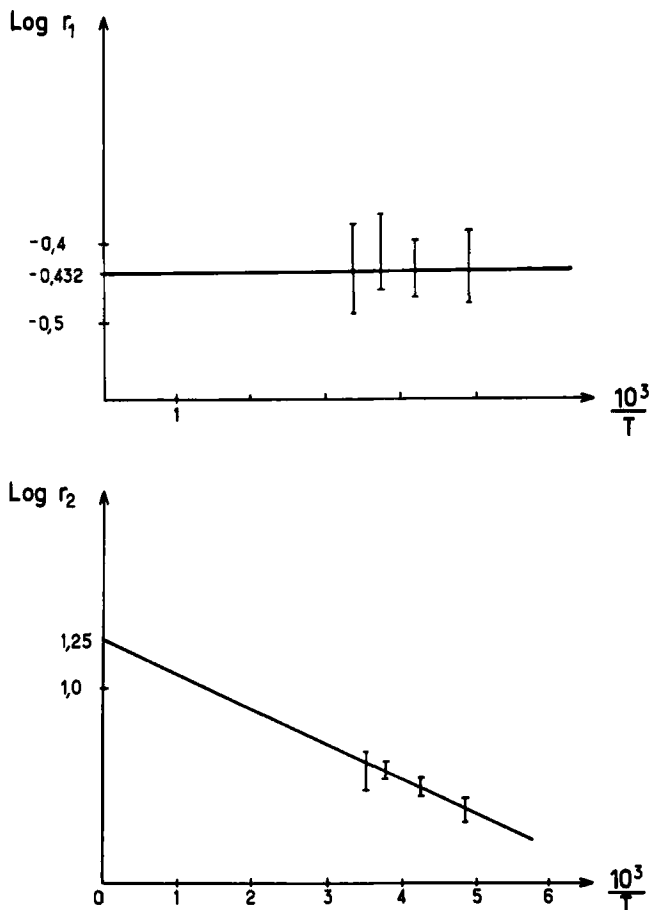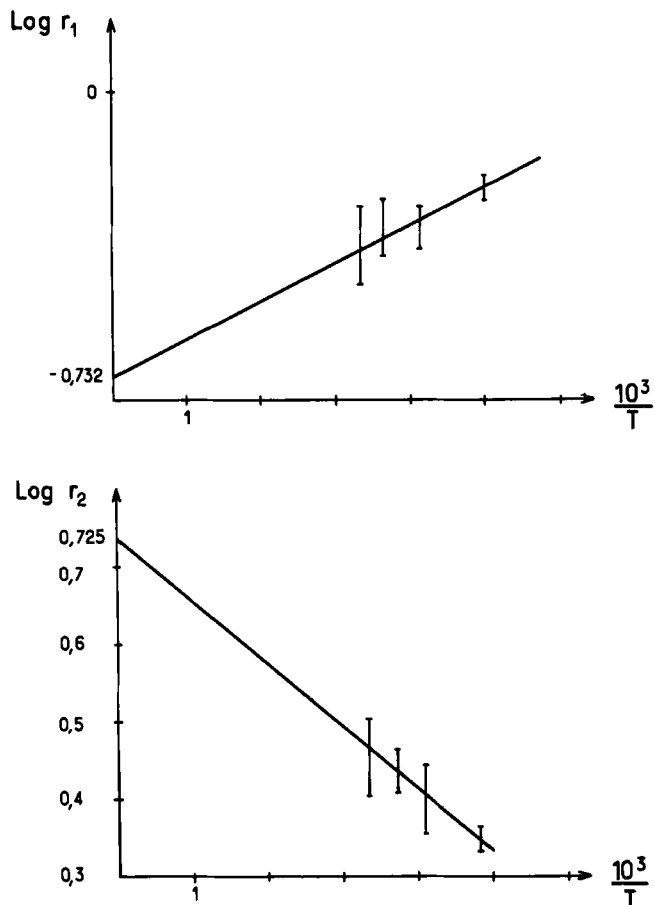
FIG. 3. Variation of $\log r_1$ and $\log r_2$ with $10^3/T$ (°K): (1) 4-chloro-styrene; (2) styrene. [$TiCl_4$] = 0.003 mole/liter; [M] = 0.1 mole/liter; solvent, CH_2Cl_2.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, that is, $\Delta H^{\ddagger} = \beta \Delta S^{\ddagger}$, where β is the isokinetic tempera-ture which can be calculated from Fig. 4: $\beta = 151°K$ or $-122°C$. The value is obtained with an accuracy of $\pm 5°K$. The existence of an iso-kinetic temperature is possible only if the two reactions are the same (that is, if the nature of the active species is the same); consequently, this proves that the reactivities of the two monomers estimated from
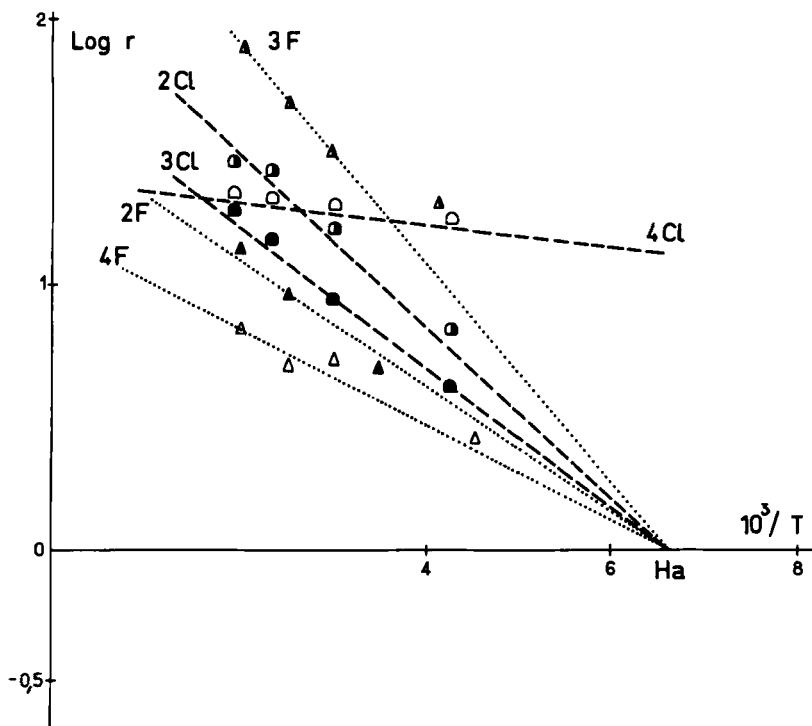
FIG. 4. Variation of log r_2 with $10^3/T$ for 2-chloro- (2Cl), 3-chloro- (3Cl), 4-chloro- (4Cl), 2-fluoro- (2F), 3-fluoro (3F), and 4-fluoro (4F) styrene. The experimental conditions are the same as for Figs. 1-3.

the $1/r_2$ values are really relative to the same active species (styryl cation in the same state of association with the counter anion) and can be reasonably compared. On the other hand, for the same mono-mers no enthalpy-entropy relationship can be found when log r_1 is plotted against $10^3/T$; this is in agreement with the fact that each reaction is relative to a particular active center. The case of the 4-chlorostyrene is special; not only does the isokinetic relation not hold for this monomer, but the variation or r_2 with the polymeriza-tion temperature is much less important than with the two other monomers. The same phenomenon was observed by Overberger but

TABLE 6. Effect of Polymerization Temperature on 4-Chlorostyrene (1)-Styrene (2) System[a]

$\theta°(°C)$	r_1	r_2	$1/r_2$	$r_1 r_2$
25	0.4 ± 0.2	3.9 ± 0.9	0.25	1.6
0	0.40 ± 0.09	3.8 ± 0.3	0.26	1.5
-30	0.40 ± 0.06	3.5 ± 0.4	0.28	1.4
-75	0.54 ± 0.02	3.33 ± 0.06	0.30	1.8

[a][$TiCl_4$] = 0.03 mole/liter; [M] = 0.1 mole/liter; solvent CH_2Cl_2.

TABLE 7. Values of r_1 and r_2 Found in the Literature for the Copolymerization of Various Chlorostyrenes (M_1) and Styrene (M_2)

M_1	Initiator	Solvent	Temperature (°C)	r_1	r_2	Reference
4-Cl	$TiCl_4$	$C_6H_5NO_2$	0	0.45	2.2	[11]
	$TiCl_4$	$C_6H_5NO_2$	5	0.43	1.9	
4-Cl	$SnCl_4$	$(CH_2Cl)_2$	30	0.35	2.7	[15]
	$TiCl_4$	CH_2Cl_2	25	0.4	3.9	
4-Cl	$EtAlCl_2$	CH_2Cl_2	0	0.64	0.80	[6]
	$TiCl_4$	CH_2Cl_2	0	0.40	3.8	
3-Cl	$SnCl_4$	$CCl_4/C_6H_5NO_2$	0	0.3	3.3	[10]
	$TiCl_4$	CH_2Cl_2	0	0.38	3.2	
2-Cl	$SnCl_4$	(CH_2Cl_2)	30	0.5	1.6	[15]
	$TiCl_4$	CH_2Cl_2	25	0.8	4.3	

with other experimental conditions [9-11]. The values of r_1, r_2 found by several authors working with various experimental conditions are reported in Table 7.

   Our results are in agreement with this set of values, except for the data of Nasirov and Plesch [6].

From the values of $\Delta H_{ii}^{\ddagger} - \Delta H_{ij}^{\ddagger}$ and $\Delta S_{ii}^{\ddagger} - \Delta S_{ij}^{\ddagger}$ the values of the reactivity ratios can be calculated [Eqs. (3)].

$$r_{2Cl-S} = 0.7$$

$$r_{S-2Cl} = \exp\{2.8 - (400/T)\}$$

$$r_{3Cl-S} = 0.37$$

$$r_{S-3Cl} = \exp\{2.6 - (400/T)\}$$

$$r_{4Cl-S} = \exp\{-1.7 + (215/T)\}$$

$$r_{S-4Cl} = \exp\{1.7 - (95/T)\} \tag{3}$$

From these relations it appears that the choice between the two monomers with the same carbocation depends mainly on entropy. This would be in agreement with a reaction very sensitive to solvent effects and to phenomena related to complex formation between the active species and the monomers. The values of $1/r_2$ calculated from these relations are given in Eqs. (4).

$$1/r_{S-2Cl} = \exp\{-2.8 + (400/T)\}$$

$$1/r_{S-3Cl} = \exp\{-2.6 + (400/T)\}$$

$$1/r_{S-4Cl} = \exp\{-1.7 + (95/T)\} \tag{4}$$

Depending on whether the preexponential or the exponential term is taken into consideration the following order of reactivity is obtained.
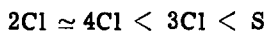
Exponential term:

4 Cl < 2 Cl ≤ 3Cl

Preexponential term:

2Cl < 3Cl < 4Cl

$1/r_2$ values:

2Cl $\simeq$ 4Cl < 3Cl < S

The comparison of these three classifications shows that the entropic terms have the most important effect and that the electronic structure also contributes to the reactivity.

Nature of the Initiator

We have used both a Lewis acid (TiCl$_4$) and a stable carbocation $(C_6H_5)_3C^{\oplus}$, SbF$_6^{\ominus}$. In the following the results obtained for the copolymerization of the three chlorostyrenes with styrene when the initiator is either TiCl$_4$ of $(C_6H_5)_3C^{\oplus}$ SbF$_6^{\ominus}$ are compared.

On the basis of a preliminary study the following experimental conditions were selected: solvent, CH$_2$Cl$_2$; temperature, 25°C; [M] = 0.1 mole/liter; [TiCl$_4$] = 0.003 mole/liter. When the initiator is $(C_6H_5)_3C^{\oplus}$SbF$_6^{\ominus}$, its concentration has a minimum value allowing the copolymerization to procede in a reasonable time. The results are reported in Table 8.

Comparison of the results obtained with TiCl$_4$ and $(C_6H_5)_3C^{\oplus}$SbF$_6^{\ominus}$ shows that in the case of 3- and 4-chlorostyrenes the influence of the nature of the initator (and consequently of the counter ion) is negligible. For 2-chlorostyrene an increase of the reactivity towards styryl cation is observed when the initiator is $C_6H_5C^{\oplus}$,SbF$_6^{\ominus}$ ($1/r_2$ = 0.91) instead of TiCl$_4$ ($1/r_2$ = 0.23). This is probably due to the fact that when there is a chlorine in the ortho position the association of the cation with the counteranion is not so close when the initiator is $(C_6H_5)_3C^{\oplus}$, SbF$_6^{\ominus}$ as when it is TiCl$_4$.

Fractionation of Copolymer

This study has been done for the following reasons: when the copolymer is precipitated from the polymerization solution, a very small

TABLE 8. Values of the Reactivity Ratios for the Copolymerization of Chlorostyrenes (M_1) with Styrene (M_2)

θ (°C)	Initiator	$[A]$ $\times 10^4$	M_1	r_1	r_2
25	$TiCl_4$	30	2-ClSt	0.8 ± 0.1	4.3 ± 0.3
25	$(C_6H_5)_3C^\oplus SbF_6^\ominus$	3	2-ClSt	0.55 ± 0.07	1.1 ± 0.1
25	$TiCl_4$	30	3-ClSt	0.37 ± 0.05	3.7 ± 0.1
25	$(C_6H_5)_3C^\oplus SbF_6^\ominus$	1.5	3-ClSt	0.50 ± 0.04	3.5 ± 0.1
25	$TiCl_4$	30	4-ClSt	0.4 ± 0.2	3.9 ± 0.9
25	$(C_6H_5)_3C^\oplus SbF_6^\ominus$	1	4-ClSt	0.64 ± 0.07	4.0 ± 0.3
10	$(C_6H_5)_3C^\oplus SbF_6^\ominus$	1	4-ClSt	0.7 ± 0.1	3.6 ± 0.2

amount of oligomers is not precipitated in some cases. If the composition of the copolymer is largely dependent on the chain length, the fact that this small fraction of polymer is not accounted for could introduce an error.

In order to ascertain to what extent the composition of the copolymer depends on the chain length, we determined the composition of the various fractions obtained from a sample by preparative gel-permeation chromatography. The samples studied are copolymers of 4-chlorostyrene and styrene copolymerized under various conditions. The conditions of copolymerization, the composition of the monomer feed and the yield are reported in Table 9.

The copolymers were fractionated and analyzed as described in the experimental section. The results are given in Table 10.

Comparison of Experimental and Theoretical Results

The comparison of the activation enthalpies and entropies for the reactions of the monomers with the styryl cation, of the $1/r_{sj}$ values, and of the stabilization energies (ΔE) for the same reaction provides the results given in Eqs. (5)-(8).

$$-\Delta H_{SS}^{\ddagger} < -\Delta H_{S-4Cl}^{\ddagger} < -\Delta H_{S-3Cl}^{\ddagger} \leq -\Delta H_{S-2Cl}^{\ddagger} \tag{5}$$

TABLE 9. Experimental Conditions for Preparation of Various
Samples of 4-Chlorostyrene Copolymers[a]

Sample number	Solvent	Molar fraction[b] M_1	Time (min)	Yield (%)
1	$C_2H_4Cl_2$	0.25	2	80
2	$C_2H_4Cl_2$	0.50	5	78
3	$C_2H_4Cl_2$	0.75	16	75
4	CH_2Cl_2	0.50	5	64
5	CH_2Cl_2	0.75	11	63

[a] $[TiCl_4]$ = 0.01 mole/liter; $[M]$ = $[M_2 + M_1]$ = 0.02 mole/liter, θ = 0°C.
[b] Fraction of M_1 in the monomer feed.

$$\Delta S_{S-2Cl}^{\ddagger} < -\Delta S_{S-3Cl}^{\ddagger} < \Delta S_{S-4Cl}^{\ddagger} < \Delta S_{S-S}^{\ddagger} \tag{6}$$

$$1/r_{S-2Cl} \simeq 1/r_{S-4Cl} < 1/r_{S-3Cl} < 1/r_{S-S} \tag{7}$$

$$(\Delta E)_{S-2Cl} = (\Delta E)_{S-4Cl} < (\Delta E)_{S-S} = (\Delta E)_{S-3Cl} \tag{8}$$

The comparison of (7) and (8) is satisfying. However according to O'Driscoll, Yonezawa, and Higashimura [16], the value of log k_{ij} is given by Eq. (9),

$$\log k_{ij} = -\Delta S_{ij}^{\ddagger}/R - [(\Delta E)_{ij} + a(\Delta E)_{ij}^{\pi}]/RT \tag{9}$$

where $(\Delta E)_{ij}$ and $(\Delta E)_{ij}^{\pi}$ are respectively the stabilization energy and π transition energy relative to the reaction of cation i with monomer j, and K_{ij} is the rate constant for the reaction. $(\Delta E)_{ij}^{\pi}$ is defined by Eq. (10)

$$(\Delta E)_{ij}^{\pi} = 2 \sum_{j}^{occ} \frac{(C_r^{j} + C_s^{j} + \cdots)^2}{\epsilon^{\oplus} - \epsilon_j} \gamma^2 \tag{10}$$

where ϵ_j and $\epsilon_j^\oplus$ represent the energy levels for the j-th molecular orbital of the monomer and for the lowest vacant orbitals of a propagating carbocation respectively and $C_r^{\ j}$ represents the coefficients of the r-th p-π orbital in the j-th molecular orbital of the monomer. γ is a resonance integral between monomer and ion and Σ_j^{occ} denotes the summation over the orbitals occupied by electrons among the molecular orbitals of monomers.

a in Eq. (9) is a constant depending on the nature of the solvent and of the initiator. In Table 11 the values of $(\Delta E)_{ij}^{\ \pi}$ are reported for the various monomers and cations studied. The values have been determined according to the various types of coordination between the cation and the monomer described by Higashimura [17], Fueno [18], and Okuyama [19].

Monocoordination:
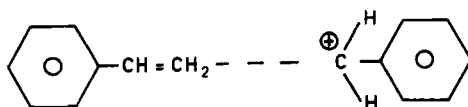
Bicoordination:
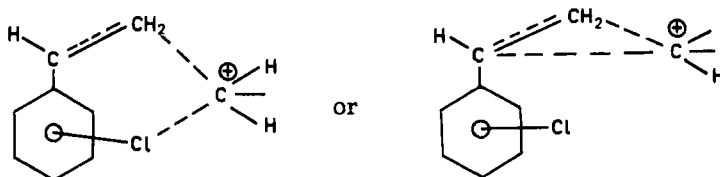
The hypothesis of a coordination between the carbocation and C7 is not improbable, since the total electronic charge of these two atoms are very closed and their superdelocalizability not drastically different.
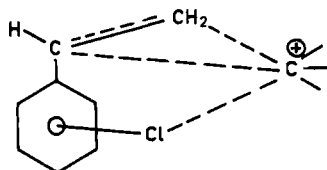
Tricoordination:

TABLE 10. Composition of the Fractions Obtained by Gel-Permeation Chromatography from Various Samples of Poly(4-chlorostyrene-co-Styrene)[a]

Fraction number	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	x (%)	m_1	x (%)	m_1	x (%)	m_1	x (%)	m_1	x (%)	m_1
1	4	15.2	2	35.7	2	63.2	4	30.2	18	59.0
2	8	15.7	2	38.0	6	66.0	7	32.2	22	61.7
3	17	16.5	6	38.0	17	69.7	13	36.0	21	62.2
4	20	17.5	15	41.5	18	70.2	20	38.7	20	63.5
5	17	20.2	16	42.7	19	75.0	23	39.2	14	63.5
6	12	22.2	22	42.7	18	75.0	14	40.0	3	67.5
7	7	23.7	17	47.0	9	73.4	8	40.7	0.5	62.7
8	3	21.0	6	49.7	6	73.0	8	39.0	0	–
9	3	19.5	6	44.5	2	70.0	0.5	35.5	0	–
10	1	17.0	4	44.2	1	62.5	0	–	0	–

[a] x is the percentage of its fractions relative to total copolymer weight; m_1 is the molar fraction of 4-chlorostyrene in each fraction of copolymer.

TABLE 11. Values of Stabilization Energy Calculated According to Eq. (10) for Various Chlorinated Monomers and Cations

	Stabilization energy			
	$S^{\oplus}$	$2\text{-}Cl^{\oplus}$	$3\text{-}Cl^{\oplus}$	$4\text{-}Cl^{\oplus}$
Coordination with C8 Only				
S	1.094	1.116	1.094	1.116
2-Cl	1.082	1.103	-	1.103
3-Cl	1.093	-	1.094	-
4-Cl	1.080	1.100	-	1.100
Coordination with Both Cl and C8				
2-Cl	2.483	2.523	-	2.523
3-Cl	2.122	-	2.122	-
4-Cl	1.838	1.844	-	1.844
Coordination with Both C7 and C8				
S	3.656	3.721	3.656	3.721
2-Cl	3.629	3.693	-	3.693
3-Cl	3.655	-	3.655	-
4-Cl	3.630	3.692	-	3.692
Coordination with C7, C8, and Cl				
2-Cl	5.135	5.292	-	5.292
3-Cl	4.701	-	4.701	-
4-Cl	4.303	4.335	-	4.335

The probability of existence of each kind of coordination will not depend only on the electronic characteristics of the coordinated atoms but also and in a large extent on the geometry of the molecule that is on the position of Cl.

According to O'Driscoll et al. [16] and to the nature of the solvent and of the initiator, 0.6 is a reasonable value for a. From Tables 2 and 11 and from a, the values of $A = (\Delta E)_{ij} + a(\Delta E)_{ij}^{\pi}$ for the various reactions have been calculated and are reported in Table 12.

TABLE 12. Values of A $(\Delta E)_{ij} + a(\Delta E)_{ij}$ Calculated According to Eq. (10) for Various Chlorinated Monomers and Cations

	A			
	$S^{\oplus}$	$2\text{-}Cl^{\oplus}$	$3\text{-}Cl^{\oplus}$	$4\text{-}Cl^{\oplus}$
Coordination with C8 Only				
S	1.463	1.470	1.463	1.485
2-Cl	1.448	1.454	-	1.468
3-Cl	1.463	-	1.463	-
4-Cl	1.447	1.451	-	1.466
Coordination with Both Cl and C8				
2-Cl	2.289	2.306	-	2.320
3-Cl	2.080	-	2.080	-
4-Cl	1.902	1.897	-	1.912
Coordination with Both C8 and C7				
S	3.001	3.083	3.001	3.048
2-Cl	2.976	3.008	-	3.022
3-Cl	3.000	-	3.000	-
4-Cl	2.977	3.006	-	3.021
Coordination with C7, C8, and F				
2-Cl	3.880	3.967	-	3.981
3-Cl	3.628	-	3.628	-
4-Cl	3.381	3.392	-	3.407

According to Eq. (5) the experimental values of $-\Delta H_{ij}^{\ddagger}$ decrease in the following order:

$$-\Delta H_{SS}^{\ddagger} < -\Delta H_{S\text{-}4Cl}^{\ddagger} < -\Delta H_{S\text{-}3Cl}^{\ddagger} \leq -\Delta H_{S\text{-}2Cl}^{\ddagger}$$

The only possibility of obtaining the same order for the relative values of $-A = -(\Delta E)_{ij} - a(\Delta E)_{ij}^{\pi}$ results from the following choice of values:

$$-A_{S-S}(-3.001) < -A_{S-4Cl}(-2.977) < -A_{S-2Cl}(-2.289)$$

$$< -A_{S-3Cl}(-2.080)$$

According to Table 12 each of these values corresponds to a particular type of coordination, namely: A_{S-S}, coordination with C8 and C7; A_{S-4Cl}, coordination with C8 and C7, A_{S-2Cl}, coordination with C8 and Cl.

The same types of coordination were suggested previously for various fluorostyrenes by Laval and Marechal [5]. For the same reasons as before and according to Furukawa [18] and Fueno [19], the tricoordination would be doubtful. On the other hand the probability of coordination of the carbocation with C8 and Cl in the case of 4-chlorostyrene is very small, due to the large distance between the two atoms. To the contrary, coordination of the carbocation with both Cl and C8 when the monomer is 2-fluorostyrene is very probable both for electronic and steric reasons. According to molecular models, coordination of the carbocation with C8 and C7 is not impossible for the 3-chlorostyrene but there is no direct proof that it occurs. However, except perhaps for 3-chlorostyrene, it appears that the values calculated for the various bicoordinations are in close agreement with our experimental determinations and correspond to the most reasonable choices.

Now, it is interesting to compare the values calculated for A with the direction of variation of the product $r_{ij}r_{ji}$. According to Tables 4-6 the quantity $r_{ij}r_{ji}$ increases with T for 2-chloro- and 3-chlorostyrenes and is roughly independent of T for 4-chlorostyrene.

Now the value of $r_{ij}r_{ji}$ is related to T by:

$$r_{ij}r_{ji} = C \exp\left\{ -[\Delta H_{ii}^{\ddagger} - \Delta H_{ij}^{\ddagger} + \Delta H_{jj}^{\ddagger} - \Delta H_{ji}^{\ddagger}]/RT \right\}$$

and $\partial(r_{ij}r_{ji})/\partial(1/T)$ has the same sign as:

$$-(\Delta H_{ii}^{\ddagger} - \Delta H_{ij}^{\ddagger} + \Delta H_{jj}^{\ddagger} - \Delta H_{ji}^{\ddagger})$$

According to Eq. (9) and to the definition of A, if the correlation between the experimental and the calculated values is reasonable,

TABLE 13. Relative Values of Rate Constants for the Reaction of
4-Chlorostyrene and Styrene with Br_2, ISCN (Iodine Thiocyanate),
and ArSCl (2,4-Dinitrobenzylsulfenyl Chloride)[a]

	Relative rate constants		
Monomer	Br_2[b]	ISCN[c]	ArSCl[c]
Styrene	0.085	0.25	0.086
4-Chlorostyrene	0.026	0.039	0.029

[a]Rate constants relative to rate constant of cyclohexene = 1.0.
[b]Data of Rolston and Yates [20].
[c]Data of Collin et al. [21].

$r_{ij}r_{ji}$ must increase with T when $A_{ii}-A_{ij} + A_{jj}-A_{ji}$ is positive. According to the types of coordination that we have found as the most probable:

$$A_{S-S} - A_{S-2Cl} + A_{2Cl-2Cl} - A_{2Cl-S} = 0.687 > 0$$

$$A_{S-S} - A_{S3Cl} + A_{3Cl-3Cl} - A_{3Cl-S} = 0.920 > 0$$

$$A_{S-S} - A_{S-4Cl} + A_{4Cl4Cl} - A_{4Cl-S} = 0.003 \simeq 0$$

These values are in agreement with the direction of variation of $r_{ij}r_{ji}$ with regards to the temperature.

It is of interest to compare the relative reactivity of 4-chlorostyrene towards the styryl cation with the relative rate constant found in the literature for the same compound but with other electrophilic reactions. The results are reported in Table 13.

For the fluorinated styrenes [5], a fairly linear relationship between the chemical shift of carbon 8 (^{13}C-NMR spectrum) and the value of $1/r_2$ has been found. Such a relation does not appear in the case of chlorostyrenes. The values of chemical shifts (against (CS_2 as internal reference) increase in the following order:
2-chlorostyrene (77.7) < 3-chlorostyrene (78.7) $\simeq$ 4-chlorostyrene (78.9) < styrene (80.5).

It appears that the chemical shift relative to styrene is above the others, in agreement with the reactivity calculated from $1/r_2$ values.

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