Reactivity Problems in the Cationic Polymerization of 9-Vinyl Anthracene, Vinyl Naphthalenes, and 4-Vinyl Biphenyl

Claude Bunel, Sylvain Cohen, Jean Pierre Laguerre,
and Ernest Marechal

*Institut National Superieur de Chimie Industrielle de Rouen,
B.P.08, 76130 Mont Saint Aignan, France.*

ABSTRACT: The cationic polymerization and copolymerization of several vinyl aromatic monomers including 9-vinyl anthracene, vinyl naphthalenes, and 4-vinyl biphenyl have been studied. The experimental reactivities are in agreement with those calculated by quantum chemistry methods. The isomerization of the carbocation of 9-vinyl anthracene has been studied at various polymerization temperatures and it has been shown that its extent depends on this parameter. The 1-vinyl-4-methoxy naphthalene does not copolymerize with styrene; moreover, styrene does not homopolymerize in the presence of this monomer.

KEY WORDS   1-Vinyl Naphthalene / 2-Vinyl Naphthalene / 1-Vinyl-4-Methoxy Naphthalene / 9-Vinyl Anthracene / 4-Vinyl Biphenyl / Cationic Polymerization / Reactivity Ratios / Temperature Effect / Solvent and Counter Ion Effect / Stabilization Energy / Superdelocalizability / Complexing /

For some years we have studied the reactivity of vinyl aromatic monomers both by experimental and theoretical methods.[1] Up to now very little information has been available on the reactivity in cationic polymerization of vinyl naphthalenes, vinyl anthracenes, and vinyl biphenyls.

In the following, [A] and [M] are the initiator and the monomer concentrations (mol l^{-1}), θ the polymerization temperature (°C), $[\eta]$ the intrinsic viscosity (100 ml g^{-1}); r_1 and r_2 are the reactivity ratios: index 1 is relative to the monomer studied and index 2 to the styrene. The numbering of monomers is as follows:
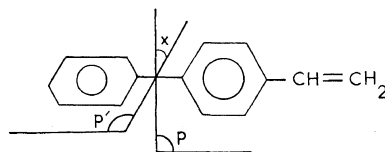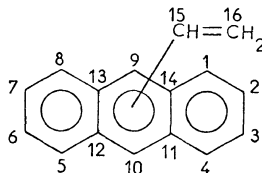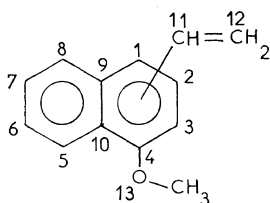
x is the angle of the two phenyl rings of biphenyl.

EXPERIMENTAL

(I) *Preparation of Monomers*

(1) 1-Vinyl naphthalene:

1-Acetyl naphthalene was reduced by AlLiH$_4$ in ether and the resulting alcohol was dehydrated by vacuum distillation on KHSO$_4$: Yield, 50; n_D^{20}, 1.6436.

(2) 2-Vinyl naphthalene:

The method described for 1-vinyl naphthalene

was applied to 2-acetyl naphthalene: Yield, 50; mp 66°C.

(3) 1-Vinyl-4-methoxy naphthalene:

The 1-acetyl-4-methoxy naphthalene was prepared by the reaction of acetyl chloride (0.5 mol) with 1-methoxy naphthalene (0.5 mol) in benzene (800 ml) in the presence of TiCl$_4$. The duration of the reaction was 2 days at room temperature: Yield, 75; mp, 71°C.

This ketone was reduced to (4-methoxy-1-naphthyl) carbinol by AlLiH$_4$ and the alcohol was distilled under vacuum to obtain 1-vinyl-4-methoxy naphthalene: Yield, 35; mp, 36°C.

(4) 4-Vinyl biphenyl:

This monomer was obtained by vacuum distillation of methyl (4-biphenyl) carbinol on KHSO$_4$: Yield, 80; mp, 120°C.

(II) *Purification of Methylene Chloride*

This solvent was refluxed, with stirring, in 20-% oleum during 24 hr. After elimination of the acidic phase the methylene chloride was washed two times by water, two times by a sodic solution, and five more times by water. The resulting solvent was distilled through a very efficient column; the purity was controlled by gas chromatography.

(III) *Purification of Initiators*

' They were distilled through a very efficient column.

(IV) *Determination of Reactivity Ratios*

They were determined by a "differential method" ($R\% \leq 8$) or by an integral method (Mayo Lewis relation). The copolymers were analysed by infrared spectroscopy.

RESULTS AND DISCUSSION

1. *Homopolymerization and Copolymerization of Vinyl Naphthalenes*

In the following, V$_1$N, V$_2$N, and V$_1$MeO$_4$N are respectively the 1-vinyl, the 2-vinyl, and the 1-vinyl-4-methoxy naphthalenes.

V$_1$N and V$_2$N have been polymerized under various conditions; the yields are most often quantitative, but the molecular weights of the relative polymers are very low ($[\eta] \simeq 0.1$).

The results are reported in Tables I, II and III.

We see that the substitution of the naphthyl ring by a methoxy group has a drastic influence

Table I. Polymerization of 1-vinyl naphthalene; influence of the nature of the initiator[a]

Initiator	[A]	Yield	$[\eta]$, 100 ml g^{-1}
Et$_2$O, BF$_3$	0.01	—	—
Et$_2$O, BF$_3$	0.05	~0	—
TiCl$_4$	0.01	90	0.07
SnCl$_4$	0.01	25	0.09
H$_2$SO$_4$	0.05	—	—
EtAlCl$_2$	0.02	70	0.10
BF$_3$ gas	—	100	0.08
AlBr$_3$	0.02	90	0.07

[a] [M], 0.15; t, 5 min; θ, −72°C; solvent CH$_2$Cl$_2$.

Table II. Polymerization of 2-vinyl naphthalene[a]

[M]	[A]	Yield	$[\eta]$, 100 ml g^{-1}
0.155	0.08	95	0.08
0.155	0.04	95	0.08
0.155	0.05	45	0.09
0.155	0.0015	5	0.10
0.28	0.01	100	0.10
0.17	0.01	100	0.10
0.11	0.01	95	0.10

[a] The initiator is TiCl$_4$ and the solvent CH$_2$Cl$_2$; θ, −72°C; t, 5 min.

Table III. Polymerization of 1-vinyl-4-methoxy naphthalene; influence of the nature of the initiator[a]

Initiator	[A]	[M]	Yield	$[\eta]$, 100 ml g^{-1}
TiCl$_4$	0.1	0.3	100	0.12
SnCl$_4$	0.1	0.3	95	0.10
BF$_3$ gas	—	0.3	100	0.24
Me$_2$O, BF$_3$	0.1	0.3	100	0.94
Et$_2$O, BF$_3$	0.05	0.36	100	0.27
Et$_2$O, BF$_3$	0.005	0.36	100	1.05
Et$_2$O, BF$_3$	0.0015	0.36	75	2.6
Et$_2$O, BF$_3$	0.0005	0.36	40	2.8
Et$_2$O, BF$_3$	0.0001	0.36	5	3

[a] Solvent, CH$_2$Cl$_2$; t, 5 min; θ, −72°C.

on the results. Thus, V$_1$N is not polymerized by BF$_3$, OEt$_2$ or BF$_3$, OMe$_2$, but V$_1$MeO$_4$N in the same conditions gives a polymer ($[\eta]$=0.94); for other initiators (with the exception of SnCl$_4$, $[\eta]$ is ten times greater with V$_1$MeO$_4$N, than with 1-vinyl naphthalene the maximum value for $[\eta]$ is 3.0 obtained with θ=−72°C, solvent CH$_2$Cl$_2$, [BF$_3$OEt$_2$]=10^{-4}, [M]=0.36.

The reactivity ratios for the various vinyl naphthalenes[1] and styrene[2] have been determined under the following conditions:

CH_2Cl_2 , $[TiCl_4]=0.003$, $\theta=-72°C$, $[M]=0.288$:
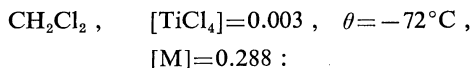
V_1N $r_1=2.6\pm0.2$ $r_2=0.33\pm0.1$

V_2N $r_1=1.75\pm0.2$ $r_2=0.75\pm0.1$

1-Vinyl-4-methoxy naphthalene does not copolymerize with styrene. Moreover, styrene does not polymerize in the presence of the methoxylated monomer or polymer unless $[TiCl_4]>$ [Methoxy].

2. Homopolymerization and Copolymerization of 9-Vinyl Anthracene (V_9A)

The polymerization of V_9A has already been widely studied.[2] However, there is a lack of information about the extent of the isomerization of the carbenium ion with respect to the temperature.

The isomerization of the carbocation and the monomer units resulting from this isomerization are described by the following scheme:

P_{12} form P_{16} form
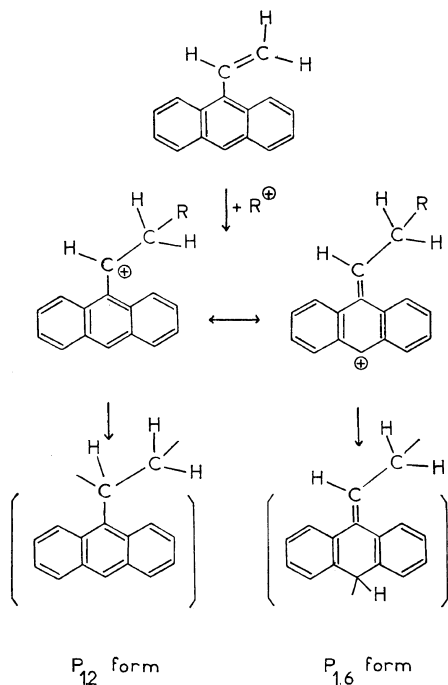
Let X be molar fraction of P_{12} form (no rearrangement), when the solvent is CH_2Cl_2, X

Table IV.

Polym. temp θ, °C	−90	−72	−50	−30	0	20	40
X	0	0	0.05	0.07	0.14	0.30	0.40

increases with θ as shown in Table IV. The pure P_{12} form was obtained only as the oligomer. The value of X was obtained by infrared analysis. The infrared spectrum of poly(9-vinyl anthracene) in the form P_{12} exhibits a band at $13.7\,\mu$ due to monosubstitued anthracene ring. This band is not present on the spectrum of P_{16} form. These two polymers exhibit the same band at $13.2\,\mu$. We used these two bands to determine x according to Michel.[2]

When the polymerization is run in nitrobenzene at 60°C, $x=0.07$.

Reactivity ratios for V_9A^1 and styrene[2] have been obtained with $[TiCl_4]=0.005$, $[M]=0.1$, $\theta=-72°C$, and CH_2Cl_2 as solvent.

$$r_1=115\pm20 ; \qquad r_2=0.10\pm0.06$$

We did not succeed in determining r_1 and r_2 for higher temperatures (e.g., 0 or 20°C), probably because in such conditions the two mechanisms contribute to the copolymerization.

The dependence of the extent of isomerization on the polymerization temperature might be due to a change of the solvatation of this cation with the temperature.

3. Copolymerization of 4-Vinyl Biphenyl (V_4B)

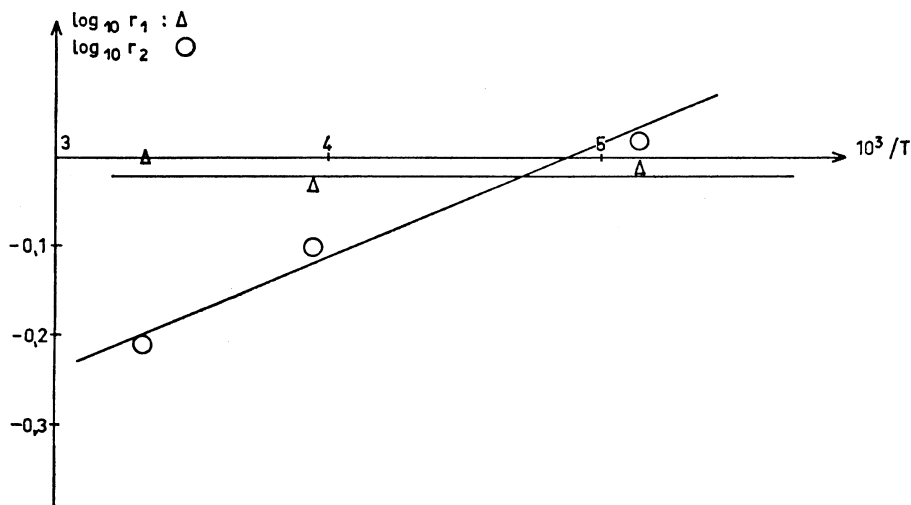Only low homopolymers ($[\eta]=0.45$) were obtained under the following conditions: CH_2Cl_2, −78°C, $[TiCl_4]=0.003$, $[M]=0.1$. V_4B has been copolymerized with styrene (index 2):

Table V.

Initiator	r_1	r_2
$TiCl_4$	0.7 ± 0.1	0.8 ± 0.1
$SnCl_4$	1.0 ± 0.1	1.4 ± 0.1

Table VI.

Solvent	$TiCl_4$	θ, °C	r_1	r_2
CH_2Cl_2	0.01	−78	0.7 ± 0.1	0.8 ± 0.1
	0.0015	25	1.0 ± 0.1	0.6 ± 0.1
$C_6H_5NO_2$	0.0015	25	1.15 ± 0.1	0.5 ± 0.1
Toluene	0.01	−78	3.6 ± 0.1	0.2 ± 0.05

Figure 1. Variations of $\log_{10} r_1$ ($\triangle$) and $\log_{10} r_2$ ($\bigcirc$) for the copolymerization of styrene (index 2) and of vinyl biphenyl (index 1) with respect to $10^3/T$ (T is the absolute temperature of polymerization).

(a) *Influence of the Nature of the Initiator.* Solvent CH_2Cl_2, $\theta = -78°C$, $[A]/[M] = 10^{-1}$.

(b) *Influence of the Nature of the Solvent.* $[M] = 0.1$.

(c) *Influence of Temperature.* Solvent CH_2Cl_2, $[M] = 0.1$, $[TiCl_4] = 0.0015$.

Reactivity ratios have been determined at various temperatures between -78 and $+25°C$. The results are reported on Figure 1. From the relation:

$$\log r_1 = (\Delta S_{11}^{\neq} - \Delta S_{12}^{\neq})/R - (\Delta H_{11}^{\neq} - \Delta H_{12}^{\neq})/RT$$

The following values were obtained:

$$\Delta S_{11}^{\neq} - \Delta S_{12}^{\neq} = -0.102 \quad \text{and} \quad \Delta S_{22}^{\neq} - \Delta S_{21}^{\neq} = -2.76$$
$$\text{(cal mol}^{-1} \text{ deg}^{-1})$$

$$\Delta H_{11}^{\neq} - \Delta H_{12}^{\neq} = 0 \quad \text{and} \quad \Delta H_{22}^{\neq} - \Delta H_{21}^{\neq} = -0.56$$
$$\text{(kcal mol}^{-1})$$

(d) *Influence of* $[A]/[M]$. Solvent CH_2Cl_2, initiator $TiCl_4$, $\theta = -78°C$. Both r_1 and r_2 decrease when $[A]/[M]$ increases, as shown in Table VII.

Table VII.

$[A]/[M] \times 10^3$	1	15	100
$r_1 \pm 0.1$	1.3	1.0	0.7
$r_2 \pm 0.1$	1.1	1.0	0.8

Theoretical Study of Reactivity—Discussion

We determined the superdelocalizability S_r on atom r and the stabilization energy $(\Delta E)_r^s$ between atom r of the monomer and the benzyl cation according to Yonezawa.[3] The results are shown in Table VIII. The units for Hückel's and Pople's values respectively, are not the same. In the case of 4-vinyl biphenyl, x (degree) is the angle of the two benzenic rings.

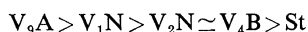The fact that Hückel's method does not take

Table VIII.

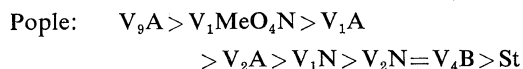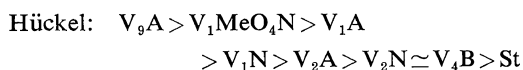| Monomer	r	Hückel		Pople $(\Delta E)_r^s$
		S_r	$(\Delta E)_r^s$	
V_1N	12	1.374	0.973	3.062
V_2N	12	1.296	0.927	3.041
V_1MeO_4N	12	1.568	1.084	—
	13	1.209	0.823	—
V_1A [a]	16	1.438	1.010	3.225
V_2A [a]	16	1.335	0.950	3.130
V_9A	16	1.601	1.106	3.487
V_4B	14	1.305	0.933	$X=0$ 3.042
				10 3.041
				20 3.041
				35 3.039
				45 3.039
Styrene		1.266	0.910	2.967

[a] V_1A and V_2A are 1-vinyl and 2-vinyl anthracenes respectively.

into account the geometry of the molecule may cause a discrepancy between experimental and theoretical results.[1,4] Now in the case of vinyl biphenyl the molecule is not planar so we determined $(\Delta E)_r^s$ by Pople's method for various values of the angle $x^{(0)}$ of the benzenic rings.

The classification of the monomers according to the value of $1/r_2$ is as follows:

$$V_9A > V_1N > V_2N \simeq V_4B > St$$

With regard to theoretical values, the classifications are:

Hückel: $V_9A > V_1MeO_4N > V_1A$
$$> V_1N > V_2A > V_2N \simeq V_4B > St$$

Pople: $V_9A > V_1MeO_4N > V_1A$
$$> V_2A > V_1N > V_2N = V_4B > St$$

There is a good level of agreement between experimental and theoretical determinations. The classification with regard to $1/r_2$ has been made for values obtained under the same experimental conditions on the values of r_1 and r_2 are under investigation for V_1N and V_2N.

As for the fact that styrene is not able to polymerize in the presence of 1-vinyl-4-methoxy naphthalene, it is interesting to compare this result with former ones. Tortai[5] found that 5MeO indene:
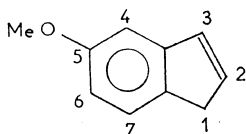
does not polymerize when θ is below a "floor value" and explained this fact by a complex formation involving oxygen atoms. This assumption was sustained both by NMR and by the superdelocalizability difference $\Delta(O—2)$ between O and C_2 atoms. (0.081). On the other hand, for 4MeO and 6MeO indenes the complex formation did not occur, but for these monomers $\Delta(O—2)$ is larger ($\simeq 0.180$). In the case of V_1MeO_4N, $\Delta(O—12)=0.359$, which is large enough to allow polymerization, but $\Delta(O—\beta)$ (between O of V_1MeO_4N and $C\beta$ of styrene) is only 0.057, which is very small; this possibly explains the inability of styrene to polymerize

in the presence of V_1MeO_4N or poly(V_1MeO_4N).[6]

Generally, for the same relative positions of the benzene rings and of the vinyl group, the reactivity increases with the number of condensed rings (VA > VN > St), but does not change very much if the two benzene rings are not condensed (V_4B slightly above St).

The examination of the variations of the reactivity ratios of the system 4-vinyl biphenyl (index 1)—styrene (index 2) with the experimental conditions leads to the following conclusion:

When the initiator is $SnCl_4$ instead of $TiCl_4$ both r_1 and r_2 increase. Now, the calculation of the stabilization energy (Table VIII) does not take into account the nature of counter ion and, in fact is done for free ions; it shows that with regard to free styryl ion the reactivity of 4-vinyl biphenyl is slightly above that for styrene. This is in agreement with the r_2 value when the initiator is $TiCl_4$; the fact that r_1 is below 1 would be due to a steric hindrance between the 4-vinyl biphenyl and the system: 4-vinyl biphenyl cation-counter ion. In the case of $SnCl_4$, there is a discrepancy between the values of r_1 and r_2. If we suppose that the association between the carbocation and the counter ion is looser in that case than when the initiator is $TiCl_4$, the value of r_1 is reasonable and in agreement with molecular orbital calculations, but r_2 should be at least below 0.8 and not equal to 1.4. On the contrary, if the ion pair is more closely associated with $SnCl_4$ than with $TiCl_4$, r_2 would be a reasonable value since the steric hindrance would disadvantage 4-vinyl biphenyl, but r_1 should be below 0.7 and not equal to 1.

The influence of the solvent depends both on dielectric constant and solvatation effects. With a very polar solvent such as $C_6H_5NO_2$ the ion pair is loose and the reactivity is not affected by steric effects, in agreement with r_1 and r_2 values; with CH_2Cl_2, when the carbocation is 4-vinyl biphenyl one, there is a slight steric hindrance since $r_1 < 1$.

When the solvent is toluene the ion pair is tighter than with the two other solvents. So, according to our previous explanations, we would expect $r_1 < 1$ and $r_2 > 1$. In fact we observe the opposite. But since the ability of toluene to solvate is very low the solvatation of the ion pair is mainly due to 4-vinyl biphenyl. Then

there is an increase of the concentration of this monomer in the neighborhood of the carbocation and an apparent increase of its reactivity.

The behavior of the system 4-vinyl biphenyl[1] styrene[2] with regards to [A]/[M] is very interesting, even if it is not easy to explain. When the relative concentration of [A] increases, both the reactivity of styrene towards vinyl biphenyl cation and of 4-vinyl biphenyl towards styryl cation increase.

The enthalpy of activation for the reaction of 4-vinyl biphenyl with styryl cation can be obtained from the relation:

$$\Delta H_{22}^{\neq} - \Delta H_{21}^{\neq} = -0.56 \text{ kcal mol}^{-1}$$

If the value of $\Delta H_{22}^{\neq}$ is assumed to be 8.1 kcal mol^{-1}[7] it results: $\Delta H_{21}^{\neq} \simeq 8.6$ kcal mol^{-1}. In the same reference a value of the frequency factor A_{22} for the polymerization of styrene is reported: $\log A_{22} \simeq 7.5$. ($l \cdot \text{mol}^{-1} \text{sec}^{-1}$) Then it is possible to obtain the equation describing the variations of the rate constant k_{SB} relative to the reaction of styryl cation with 4-vinyl biphenyl with regard to temperature:

$$k_{SB} = 1.25 \times 10^{8} \exp{(-4330/T)} \quad (l \text{ mol}^{-1} \text{ sec}^{-1})$$

The same relation for the reaction of styrene with its own cation is:

$$k_{SS} = 3.2 \times 10^{7} \exp{(-4080/T)} \quad (l \text{ mole}^{-1} \text{ sec}^{-1})$$

We observe that the frequency factors, the energies of activation and $1/r_2$ are in the same relative position:

4-vinyl biphenyl > styrene
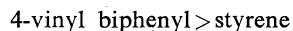
The stabilization energies are also in the same relative position (Table VIII).

BIBLIOGRAPHY

1. E. Marechal, *J. Macromol. Sci.*, **A7**, 433 (1973).
2. R. H. Michel, *J. Polym. Sci., Part A1*, **2**, 2533 (1964); A. Rembaum and A. Etsenberg, *Makromol. Rev.* **1**, 57 (1967).
3. K. F. O'Driscoll and T. Yonezawa, *Rev. Macromol. Chem.*, **1**, 1 (1966).
4. S. Cohen, P. Belliard, and E. Marechal, *Polymer*, **14**, 352 (1973).
5. J. P. Tortai and E. Marechal, *Bull. Soc. Chim. Fr.*, 2673 (1971).
6. M. Mayen and E. Marechal, *ibid.*, 4662 (1972).
7. T. Higashimura, Structure and Mechanism in vinyl polymerization, Dekker, 1969, p 329.