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Influence of the Nature and Position of Substituents on the Cationic Polymerization of Some Aromatic Monomers

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ABSTRACT

The cationic polymerization of methylated and methoxylated monomers was studied by two methods: determination of experimental reactivity and theoretical study of the monomers using quantum chemistry. There was often very good agreement between the results obtained with each methods. Nevertheless, in several cases the discrepancy between theoretical and experimental values indicated some side phenomena: preliminary isomerization of the monomer, the effect of ring strain, the effect of a substituent on the planarity of monomers, and formation of a complex. This last phenomenon was extensively studied through an examination of NMR spectra of the polymerization solution at low temperature. For the quantum chemistry study, Hückel's method was essentially used. However, some studies were also made by Pople's method.

INTRODUCTION

For many years the cationic polymerization and copolymerization of vinyl monomers in the series of indene, styrene, and acenaphthylene has been studied. The purpose of these studies was primarily the determination of the electronic and steric effects of substituents on the ability of the substituted monomers to be polymerized. Different kinds of substituents were considered: methyl, methoxy, and halogens. However, this paper is essentially concerned with the influence of methyl and methoxy group.

To study these polymerizations, two methods were used:

1) An experimental method in which the influence of several parameters on the polymerization was studied: monomer and initiator concentration, nature of solvent, nature of initiators, duration of polymerization, and temperature. An important part of this work was the determination of the reactivity ratios for each monomer in regard to a reference monomer. For example, in the indene series the reactivity ratios of different methyl indenes were determined through their copolymerization with indene and styrene.

2) A theoretical method in which the electronic characteristics of the monomers and eventually of the cations were determined through quantum chemistry. Previously, Hückel's method was mostly used, but more recently Pople's method (CNDO II) has become more precise and this new technique has already yielded interesting data.

THEORETICAL STUDIES

Methods Employed and Critical Evaluation of Their Utilization

Until now, Hückel's method has essentially been used but more recently Pople's method has become more popular.

Hückel's Method

This is the most commonly used method in quantum chemistry but very often too much is expected from Hückel's method and it is impossible to consider the data obtained to be of any value. In this method (as in Pople's) the molecular orbital Ψ_j is a linear combination of atomic orbitals χ_i: $\Psi_j = \Sigma C_{ij}\chi_i$ and is linked to the energy value E_j through the relation

$$H\Psi_j = E\Psi_j$$

in which H is the classical Hamiltonian operator. The values of E_j (eigenvalues) and of C_{ij} (eigenvectors) are obtained by an application of the variation principle.

In this application, several integrals appear:

$$\int \chi_i \chi_j \, d\tau = \int \chi_j \chi_i \, d\tau = s \qquad \text{(overlap integral)}$$

$$\int \chi_i H \chi_j \, d\tau = \int \chi_j H \chi_i \, d\tau = H_{ij} \qquad \text{(resonance integral)}$$

$$\int \chi_i H \chi_i \, d\tau = H_{ii} \qquad \text{(Coulomb integral)}$$

In Hückel's method the integrals are not calculated but treated as parameters. The diagonal element H_{ii} is supposed to have a value α_i characteristic of its own atomic orbital χ_i. H_{ii} is supposed to be independant of the rest of the molecule. The off diagonal element H_{ij} is called the resonance integral and is assumed to have a value β_{ij} characteristic only of the atomic orbital χ_i and χ_j, and if χ_i and χ_j are atomic orbitals of two atoms which are not linked by a covalent bond, $\beta_{ij} = 0$.

For a carbon atom and a C—C bond, the commonly used notations are $\beta_{ij} = \beta$ and $\alpha_{ij} = \alpha$. Hückel's method employs some very rough approximations. The most important criticism is that the total binding energy of the molecule:

$$E_{tot} = 2 \sum_{j}^{occ} E_j$$

is assumed to be equal to the total energy of the electrons. In fact, in an orbital representation the total electronic energy is not the sum of the orbital energies; the total average electronic repulsion has to be substrated from this sum and the total internuclear repulsion added. Moreover, the assumption that H_{ii} and H_{ij} only depend on χ_i and χ_j and not on the rest of the molecule is more intuitive than the result of rigorous justification. Finally, Hückel's method is not self-consistent since it neglects electron spin although a form of the one electron Hamiltonian is used. This can only be justified if the electron spin is taken into account. Nevertheless, Hückel's method has been widely applied and very often there has been quite good (sometimes extremely good) agreement between experimental and theoretical results.

This method can be very useful if it is used with care. First, this work was carried out with planar conjugated molecules and more often with benzoic alternant hydrocarbons. Second, this method was used for qualitative or semiquantitative studies. For example, with Yonezawa's relation [1, 2] for the determination of stabilization energies $(\Delta E)_r^s$ of methyl indenes, the values of $(\Delta E)_r^s$ were not assumed to have an absolute signification. This assumption would be meaningless because two or three parameters have to be chosen to treat indene and the methyl group. But since the values of these parameters remained constant for all the series, the classification of methyl indenes with respect to the values of $(\Delta E)_r^s$ was quite valuable. The experimental results confirmed this hypothesis.

When the system was no longer completely conjugated or if methyl groups or hetero atoms were included, the values of α_i and β_{ij} had to be modified for the atoms involved in this modification. To perform this adjustment, some corrective parameters were employed. For example, if a hetero atom or a methyl group, X, is linked to a carbon atom $(X{-}C\lessgtr)$ the Coulomb's integral α_i and the resonance integral β_{ij} for these two atoms are expressed by

$$\alpha_X = \alpha + \delta_X \beta$$

$$\alpha_C = \alpha + \delta_C \beta$$

$$\beta_{CX} = \rho_{CX} \beta$$

in which δ_X and ρ_{CX} are parameters chosen to give the best account for the properties of the considered molecules. The problem of the choice of the values of these parameters has been studied by numerous authors, but the solution has not been satisfying in all cases. Very often a parameter chosen for a definite property (chemical reactivity, electronegativity) is not convenient enough to yield a reasonable quantitative interpretation of another property. Therefore it was concluded that it would not have been significant to multiply the number of parameters with respect to the problem studied.

Nevertheless, if the same parameters were kept for the same kind of substituent, the classification of the monomers with respect to the relative values of $(\Delta E)_r^s$ was very valuable. However, it must be emphasized again that the values obtained cannot be seriously used as having an absolute significance.

Throughout this study only the values obtained for compounds with the same structure were compared. For example, a comparison between the methyl indenes, or the methoxyindenes, or the methoxystyrenes was valuable, but there was little significance in comparing methoxyindenes with methoxystyrenes or even indene with styrene. Since it is not possible to extrapolate from one system to another, the fact that a given choice of Hückel's parameters fits well for one set of compounds is not a justification to use it for compounds of another type.

In working with cations the basic assumption that the total interelectronic and internuclear repulsions cancel is patently incorrect. Therefore, care was taken to always use the same cation (benzyl) so as not to change the magnitude of this approximation.

Another problem with Hückel's method comes from the fact that the molecular geometry cannot be taken into account and therefore the neglect of ring strain in acenaphthylene prevents good agreement between experimental and theoretical results.

Pople's Method

Details of Pople's method have been given in numerous publications [3-6]. In this method, as in Hückel's method, the molecular orbitals are expressed as linear combinations of atomic orbitals. When the coefficients in the linear combinations are chosen to minimize the total energy, LCAO SCF orbitals are obtained. SCF means that it is a self-consistent field method. The first relations for this problem were developed by Hall [7] and Roothaan [8], and a large number of accurate calculations have been made for small molecules by using this technique. But the use of this method for larger systems is limited by computational difficulties. Moreover, it is important to extend the molecular calculations to all electronic valences and not only to use π electrons. This improvement in the method allowed a complete treatment of the σ and π electrons in planar molecules, especially for those in which σ and π systems are not separable.

Pople imagined a consistent field method which took account of σ and π valence electrons, but the differential overlap was completely neglected (CNDO) for all valence orbitals. Therefore, the extension of such a method to large systems could be considered.

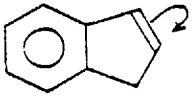
An improvement of the first version of the CNDO method (CNDO I) [4] was described in a third publication (CNDO II). This method was easily extended to open shells of electrons.

In employing this method, a listing for the CNDO II approximations, programmed by Segal at the Carnegie Institute of Technology, was used. This program calculates wave functions and energies for molecules in open or closed shell states. The data consist mainly in the coordinates x, y, and z of the different atoms of the molecule. The most accurate values possible for bond lengths and angles are needed. Interesting data were obtained for the systems acenaphtylene, styrene, and benzylic cation. Unfortunately, the molecular geometry of indene is not sufficiently well known at present for it to be included.

Use of Calculations

Hückel's and Pople's methods give the values of energy levels and eigenfunctions (C_{ij}). From these values it is possible to calculate several quantities which give some very important information about the monomers studied. The classical values of total charge, bond order, or free valence cannot solve every problem. Consequently, the frontier electron density and the superdelocalizability are often used [9-11]. These last values are particularly useful in determining the areas in which secondary reactions may occur. Secondary reactions are generally transfer reactions or electrophilic attacks of the benzenic ring by a cation terminating the growing chain. However, at times the value of the superdelocalizability has been essential in determining the position where the cation attacks the monomer. Generally there is no doubt about the position of attack, except in the case where a complexing group is able to fix the cation concurrently with the π bond of the vinyl group.

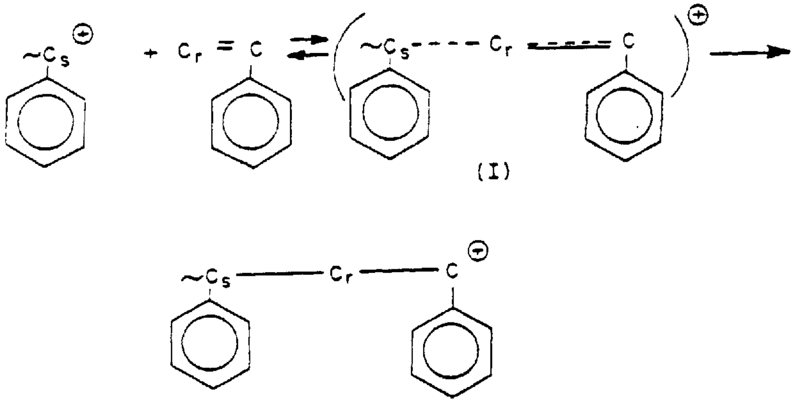
The first dynamic value considered is the localization energy L_r. L_r represents the energy required to isolate the electrons of a π bond on an atom r of the molecule. For example, the localization energy involved in the polymerization of indene is the energy necessary to isolate the π double bond between carbons 2 and 3 on carbon 2:



L_r is usually a positive quantity.

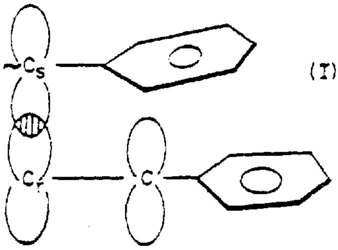
The localization energy is a mesure of the π energy change between the aromatic hydrocarbon and the σ intermediate complex in an aromatic substitution. If all the σ bond changes are treated as being constant in this transformation, a correlation between the calculated localization energies and the experimental reactivities is obtained.

Another index of the reactivity is the stabilization energy $(\Delta E)_r^s$ introduced by Yonezawa [1, 2]. $(\Delta E)_r^s$ represents the change of energy involved in the formation of an intermediary complex between at atom s of the cation on the end of the growing chain and an atom r of the monomer. The following reaction shows how this complex is formed (O'Driscoll and Yonezawa [2]).



(I)

The transition state is



(I)

The value of $(\Delta E)_r^s$ is obtained with the relation

$$(\Delta E)_{r,s} = \left(2 \sum_{m}^{occ} \sum_{n}^{unocc} - \sum_{m}^{occ} \sum_{n}^{unocc} \right) \frac{(a_r^m)^2 (b_s^n)^2 (\Delta\beta)^2}{F_n - E_m}$$

a_r^m and b_s^n are, respectively, the orbital coefficients of the carbon atoms r and s in the m-th and the n-th energy levels having E_m and F_n as energy values.

The subscripts "occ" and "unocc" mean that the summation is extended to all occupied or unoccupied orbitals. With Hückel's method $(\Delta E)_r^s$ are obtained in units of $-\Delta\beta^2/\beta$.

$\Delta\beta$ is the resonance integral of the r—s bond during the transition state (I). O'Driscoll and Yonezawa [2] analyzed the importance of $\Delta\beta$. They claim that $\Delta\beta$ is a function of the transition state separation which in turn depends on the electronic repulsion in the transition state. However, the electronic repulsion is not considered in the calculation. But it has been shown that small transition state separations have high values of $\Delta\beta$ and also high values of electronic repulsion. These effects tend to cancel each other, and it is acceptable to keep the same average value of $\Delta\beta$ for a series of monomers.

The results obtained with the monomers of several series are presented in the following pages.

The abbreviations M, D, or T indicate that the compound is mono-, di-, or trisubstituted. The numbers following this notation correspond to the atoms attached to the substituting group.

S_r represents the superdelocalizability on the atom r, L_r represents the localization energy, and $(\Delta E)_r^s$ represents the stabilization energy between the atom r of the monomer and the atom s of the cation. All the results are discussed in the section on Discussions and Conclusions.

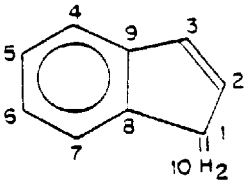
Indene and Methyl Indenes [12, 13]. Two sets of parameters were used to describe the methyl group:

1. Inductive model. $\geqslant C-Me$

$$\alpha_C = \alpha + \delta_C \beta \text{ and } \beta_{C-Me} = \eta_{C-Me}\beta$$

The classical values $\delta_C = 0.2$ and $\eta_{C-Me} = 0$ were considered.

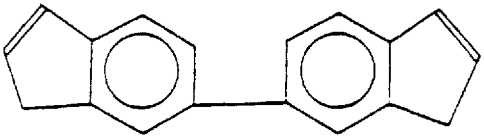
2. Hyperconjugated model. $\geqslant C_1-C_2\equiv H_3$. $\delta_{C_1} = -0.1$, $\delta_{C_2} = 0$, $\delta_{H_3} = -0.2$, $\eta_{C_1-C_2} = 0.7$, $\eta_{C_2\equiv H_3} = 2$. For the indene molecule, the numbering of the atoms is



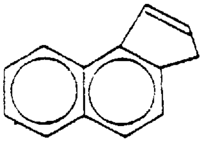
Modified values of the parameters of Pullman and Berthier's method [14] were used. These authors considered the methylene group as a double bond $C{=}H_2$ for their model of indene. The $C{=}H_2$ can be conjugated with other double bonds of the molecule. The relation $\beta' = \eta\beta$ (β is the exchange integral between C and H) expresses the delocalization of this bond. The choice of β' is obviously arbitrary, but it is possible to compare a set of indene derivatives for which the value of η may be assumed to be constant. $\eta = 3$ was chosen (literature, $\eta = 5$). In addition, $\eta = 0.7$ was taken for the bonds issuing from C_1 ($C_1{-}C_2$ and $C_1{-}C_8$).

The results for the inductive and hyperconjugated models have been previously described [12, 13]. The two models differ from one another only in the third decimal. Table 1 gives the results obtained with the inductive model.

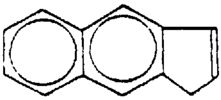
Bis Indenyls and Benzindenes [15]. Bis-indenyls are designated by the position of the linkage between the two indenyl rings. For example, the structure of bis(indenyl-6) is



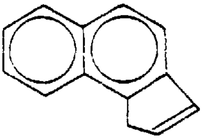
Superdelocalizability, localization energy, and stabilization energy values are tabulated in Table 2 for the following benz-indenes (Bz):



Benz-4,5 inden



Benz-5,6 inden



Benz-6,7 inden

and for several bisindinyls.

Benzofuran and Benzothiophan and Their 4- and 7-Methyl Derivatives [16]. Position 1 is indicated by the hetero-atom. The results are given in Table 3 with:

$$\eta_{O-C_2} = \eta_{O-C_8} = 0.6$$

$$\eta_{S-C_2} = \eta_{S-C_8} = 0.8$$

TABLE 1. Values of Superdelocalizabilities S_r, of Localization Energies L_r, and of Stabilization Energies $(\Delta E)_2{}^3$ for Methyl Indenes

	S_r			
	Carbon r			
Monomers	2	3	L_r	$(\Delta E)_2{}^3$
Indene	1.307	1.058	1.824	0.898
M2	1.242	1.178	-	0.891
M3	1.459	0.928	1.710	1.017
M4	1.303	0.932	1.796	0.927
M5	1.250	0.932	1.826	0.893
M6	1.303	0.932	1.794	0.920
M7	1.250	0.931	1.824	0.897
D45	1.301	0.932	1.798	0.926
D46	1.430	0.932	1.766	0.960
D47	1.301	0.930	1.798	0.926
D56	1.302	0.931	1.796	0.927
D57	1.252	0.933	1.826	0.898
D67	1.306	0.931	1.796	0.928
T456	1.357	0.932	1.768	0.958
T457	1.304	0.931	1.792	0.928
T467	1.362	0.931	1.766	0.961
T567	1.308	0.931	1.796	0.930
T4567	1.324	0.932	1.766	0.961

Methoxy Indenes [17].

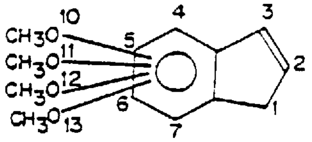


TABLE 2. Values of Superdelocalizabilities S_r, of Localization Energies L_r, and of Stabilization Energies $(\Delta E)_r^S$ for bis-Indenyls and Benz-indenes

	Atom r					
	S_r		L_r		$(\Delta E)_r^S$	
Monomers	2	3	2	3	2	3
Bz-4.5	1.359	0.918	1.758	-	0.772	-
Bz-4.6	1.280	0.930	1.806	-	0.728	-
Bz-6,7	1.281	0.929	1.802	-	9.710	-
Bi-2,2'	1.063	0.367	3.096	1.702	0.550	1.546
Bi-3,3'	0.550	0.851	1.316	3.598	1.438	0.447
Bi-4,4'	1.062	0.923	1.676	-	0.909	-
Bi-5,5'	1.250	0.931	1.826	-	0.710	-
Bi-6,6'	1.056	0.926	1.686	-	0.902	-
Bi-7,7'	1.251	0.931	1.824	-	0.710	-

TABLE 3. Values of Superdelocalizabilities S_r and of Stabilization Energies $(\Delta E)_r^S$ for Benzothiophen (Bt) and Benzofuran (Bf) and Some of Their Derivatives

	Atom r			
	Sr		$(\Delta E)_r^S$	
Monomers	2	3	2	3
Bf	1.162	1.159	0.768	0.554
Bt	1.170	1.217	0.768	-
DiMe-4, 7 Bf	1.207	1.175	0.753	0.794
DiMe-4, 7 Bt	1.212	1.236	-	0.557

The indene ring has been treated as in Part A. For the methoxy group, two sets of parameters have been chosen.

1. Results obtained with the first two parameters.

$\delta_{O-CH_3} = 2$ and $\eta_{O-CH_3} = 0.8$

The results are given in Table 4.

TABLE 4. Values of Superdelocalizabilities S_r on Atom r and of $(\Delta E)_r^s$ on Atom 2 for Several Methoxy Indenes when $\delta_X = 2$ and $\eta_X = 0.8$

	Atom r						
	S_r						$(\Delta E)_r^s$
Monomer	2	3	11	12	13	14	2
M2	1.186	1.406	1.220	-	-	-	0.851; on 3:0.968
M3	1.706	0.897	1.183	-	-	-	1.162
M4	1.360	0.927	1.181	-	-	-	0.960
M5	1.258	0.940	1.159	-	-	-	0.902
M6	1.362	0.938	1.157	-	-	-	0.961
M7	1.256	0.934	1.156	-	-	-	0.900
D45	1.360	0.930	1.214	1.201	-	-	0.960
D46	1.471	0.927	1.180	1.178	-	-	1.023
D47	1.365	0.923	1.210	1.191	-	-	0.963
D56	1.370	0.937	1.196	1.206	-	-	0.966
D57	1.259	0.941	1.155	1.157	-	-	0.902
D67	1.364	0.929	1.212	1.200	-	-	0.962
T456	1.478	0.930	1.206	1.236	1.208	-	1.028
T457	1.367	0.927	1.248	1.201	1.200	-	0.964
T467	1.482	0.918	1.212	1.212	1.227	-	1.030
T567	1.372	0.929	1.200	1.246	1.199	-	0.967
T4567	1.495	0.926	1.246	1.234	1.244	1.233	1.037
Indene	1.251	0.932	-	-	-	-	0.898

2. Results obtained with the second two parameters.

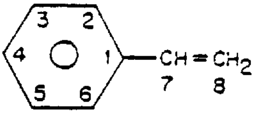
$\delta_{O-CH_3} = 1$ and $\eta_{O-CH_3} = 0.8$

The values are reported in Table 5.

TABLE 5. Values of Superdelocalizabilities S_r on Atom r and of Stabilization Energies $(\Delta E)_r^S$ on Atom 2 for Several Methoxy Indenes when $\delta_X = 2$ and $\eta_X = 0.8$

	Atom r						
	S_r						$(\Delta E)_r^S$
Monomer	2	3	11	12	13	14	2
M2	1.095	2.181	2.746	-	-	-	0.792
M3	2.447	0.853	2.661	-	-	-	1.589
M4	1.310	1.067	2.643	-	-	-	0.929
M5	1.249	0.933	2.618	-	-	-	0.896
M6	1.528	0.926	2.654	-	-	-	1.056
M7	1.249	0.932	2.617	-	-	-	0.896
D45	1.588	0.920	3.128	3.091	-	-	1.091
D46	1.832	0.916	2.646	2.647	-	-	1.231
D47	1.611	0.921	3.111	3.073	-	-	1.104
D56	1.604	0.924	3.080	3.117	-	-	1.100
D57	1.248	0.933	2.615	2.614	-	-	0.895
D67	1.605	0.924	3.123	3.083	-	-	1.101
T456	1.825	0.914	3.230	3.769	3.209	-	1.227
T457	1.703	0.921	3.812	3.204	3.184	-	1.156
T467	2.196	0.910	3.223	3.223	3.776	-	1.439
T567	1.714	0.922	3.193	3.809	3.178	-	1.162
T4567	2.190	0.908	3.801	3.768	3.801	3.772	1.435
Indene	1.251	0.932	-	-	-	-	0.898

Methyl Styrenes [18, 19]. The methyl group has been treated in the same manner as for the methyl indenes. The numbering for the molecule is



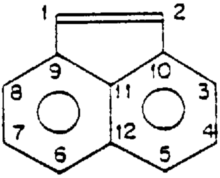
The results are reported in Table 6.

Methoxy Styrenes [20]. The following values for the methoxy group were chosen

$$\alpha_{O-CH_3} = \alpha + 1.8\beta \text{ and } \eta_{O-CH_3} = 0.8$$

The results are given in Table 7.

Acenaphthylene and Methyl Acenaphthylenes [21]. The numbering for this molecule is



The results are reported in Table 8.

EXPERIMENTAL STUDIES

It would be difficult to describe the preparation of the monomers studied since more than 50 (about 30 are new) were synthesized [16, 17, 22-41].

For each monomer a complete study of each of the important parameters for the polymerization was investigated: nature and concentration of initiator, monomer concentration, nature of solvent, temperature, and duration of reaction. Since the goal of this report is not the examination of these results, only a few examples of the most interesting results are considered.

Drastic changes are noted for some properties when, for a given basic monomer, the substituents are different, either by their place or by their nature. Tables 9, 10, and 11 show the effect of

TABLE 6. Values of Superdelocalizabilities S_r and of Stabilization Energies $(\Delta E)_r^s$ for some Methyl Styrenes

	M															
r	St	M2	M3	M4	D23	D24	D25	D26	D34	D35	T234	T235	T236	T245	T246	T345
Superdelocalizability S_r																
7	0.905	0.913	0.909	0.907	0.908	0.912	0.911	0.912	0.907	0.909	0.907	0.909	0.911	0.914	0.912	0.911
8	1.266	1.318	1.268	1.321	1.319	1.372	1.320	1.370	1.322	1.268	1.375	1.322	1.371	1.376	1.427	1.322
Stabilization Energy $(\Delta E)_r^s$																
7	0.681	0.682	0.679	0.679	0.679	0.681	0.681	0.682	0.679	0.680	0.679	0.679	0.681	0.682	0.681	0.681
8	0.910	0.939	0.911	0.941	0.940	0.970	0.941	0.969	0.942	0.911	0.972	0.942	0.969	0.972	1.001	0.941

TABLE 7. Values of Superdelocalizabilities S_r and Stabilization Energies $(\Delta E)_r^s$ for Several Methoxy Styrenes. $\alpha_X = \alpha + 1.8\beta$ and $\eta_{C-X} = 0.8$

	M														
r	St	M2	M3	M4	D23	D24	D25	D26	D34	D35	T234	T235	T236	T245	T246	T345
Superdelocalizability S_r																
7	0.905	0.911	0.917	0.912	0.909	0.907	0.913	0.913	0.915	0.919	0.906	0.909	0.906	0.908	0.907	0.914
8	1.266	1.375	1.264	1.371	1.376	1.488	1.382	1.481	1.379	1.264	1.488	1.384	1.485	1.513	1.603	1.386
Stabilization Energy $(\Delta E)_r^s$																
7	0.681	0.680	0.684	0.681	0.679	0.678	0.682	0.681	0.683	0.685	0.678	0.679	0.677	0.679	0.677	0.682
8	0.910	0.972	0.908	0.970	0.973	1.037	0.976	1.033	0.974	0.908	1.037	0.977	1.035	1.051	1.103	0.978

TABLE 8. Values of Superdelocalizabilities S_r and Stabilization Energies $(\Delta E)_r^s$ for Acenaphthylene (Ac) and some Methyl Acenaphthylenes

Monomers	Ac	M1	M3	M4	M5
S_1	1.188	1.204	1.228	1.189	1.232
S_2	1.188	1.365	1.180	1.190	1.181
$(\Delta E)_s^1$	0.847	0.949	0.869	0.848	0.877

TABLE 9. Influence of Position of Methyl Group on Polymerization of Methyl Indenes for Several Initiators[a]

Nature of initiator	Indene		D46	D47	D56	D57		T4567
	R%	$[\eta]$	$[\eta]$	$[\eta]$	$[\eta]$	R%	$[\eta]$	$[\eta]$
$TiCl_4$	100	0.56	1.35	1.30	0.39	95	0.09	0.25
$SnCl_4$	45	0.59	1.50	1.60	0.34	100	0.08	0.23
$BF_3.O(CH_3)_2$	12	-	2.50	3.60	0.46	0	-	0.26
$BF_3.O(C_2H_5)_2$	-	-	2.20	3.5	0.45	0	-	0.31
H_2SO_4	8	0.20	1.15	1.0	0.10	65	0.09	0.38
$AlBr_3$	-	-	-	-	-	100	0.12	-
$SbCl_5$	-	-	-	-	-	100	0.09	-

[a] $[M] = 0.224$, $[A] = 0.01$, and $\theta = -30°C$. Methylene chloride as solvent.

position of the methyl group in the indene and styrene series on the efficiency of several initiators. R% designates the yield of polymer precipitated by addition of methanol to the polymerization solution; $[\eta]$ represents the intrinsic viscosity (100 ml/g); $[M]$ and $[A]$ are the monomer and the initiator concentration (mole/liter), respectively, and θ is the polymerization temperature.

The most important part of this experimental study was concerned with the determination of the reactivity ratios for the substituted monomers using the basic nonsubstituted model of the same series or styrene as reference.

TABLE 10. Influence of Position of Methyl Group on Polymerization of Methyl Indenes for Several Initiators[a]

Nature of initiator	Indene	M5	M6	M7		D46	D47		D56	D57		T467
	$[\eta]$	$[\eta]$	$[\eta]$	R%	$[\eta]$	$[\eta]$	R%	$[\eta]$	$[\eta]$	R%	$[\eta]$	$[\eta]$
$TiCl_4$	1.57	0.5	2.2	100	0.82	0.95	100	1.8	0.95	95	0.15	0.83
$SnCl_4$	0.95	0.8	-	-	-	1.05	100	1.9	1.05	100	0.07	0.65
$BF_3.O(CH_3)_2$	0	-	2.7	100	0.62	2.40	45	1.5	2.40	0	-	0.95
$BF_3.O(C_2H_5)_2$	0	0.8	4.5	90	0.48	2.30	100	3.4	2.30	0	-	1.73
H_2SO_4	0.50	-	2.2	-	-	1	100	1.3	1.00	65	0.11	0.62
$AlBr_3$	-	-	-	-	-	-	-	-	-	100	0.17	-
$SbCl_5$	-	-	-	-	-	-	-	-	-	100	0.13	-

[a] [M] = 0.224, [A] = 0.01, and θ = -72°C. However, for the trimethyl-4,5,7-indene (T467), [M] = 0.422 and [A] = 0.02 when BF_3 etherates are used as initiators. For methyl-5-, methyl-6-, and methyl-7-indenes, [M] = 0.384 and [A] = 0.05 when the initiator is $SnCl_4$ or $TiCl_4$.

TABLE 11. Effect of the Position of the Methyl Group on the Polymerization of Some Methyl Styrenes with Different Initiators[a]

Nature of initiator	T246		T245		T345	
	R%	[η]	R%	[η]	R%	[η]
$TiCl_4$	100	0.44	100	0.18	94	0.08
$SnCl_4$	93	0.20	100	0.28	96	0.15
$BF_3.O(C_2H_5)_2$	90	2.7	93	0.34	96	0.14
$BF_3.O(CH_3)_2$	10	2.65	72	0.32	92	0.14
H_2SO_4	87	0.42	60	0.45	0	-
$AlBr_3$	100	0.88	97	0.08	-	-
$AlCl_3$	18	0.63	89	0.15	7	-
BF_3	100	1.80	-	-	-	-

[a] Solvent: CH_2Cl_2. [M] = 0.456 and $\theta = -72°C$. For each monomer-initiator pair, the value chosen for [A] was the optimum.

If r_1 and r_2 are the reactivity ratios for a monomer M with a reference R, the respective index 1 and 2 are given to M and R. Then

$$r_1 = kM^{\oplus}M/kM^{\oplus}R \qquad r_2 = kR^{\oplus}R/kR^{\oplus}M$$

The value of $1/r_2 = kR^{\oplus}M/kR^{\oplus}R$ measures the preference of the attack of $R^{\oplus}$ on M or its own monomer R. If $kR^{\oplus}$ is arbitrarily taken as equal to 1, then $1/r_2$ is the measure of the reactivity of M vs the cation $R^{\oplus}$. Consequently, the determination of $1/r_2$ for a set of monomers derived from an identical fundamental structure allows their classification with regard to their reactivity toward the same cation.

For example, for the methyl indene, the cation was indene. The classification does not depend on the cation, but obviously the absolute values of $1/r_2$ are modified when the cation changes.

Classification of Methyl Indenes from $1/r_2$

The given values are related to the copolymerization with indene [28, 32, 41].

D46 ≃ T4567 ≃ T467 ≃ D57	5 to 6
T47 ≃ D56 ≃ M6	2 to 3
M7	Slightly above 1
Indene	1
M5	Slightly below 1

Classification of Methoxy Indenes from $1/r_2$

The given values are related to copolymerization with styrene [17].

MeO-6	10
MeO-4	6.7
MeO-5	2.8
Indene	1.1
Styrene	1

Classification of Methyl Styrenes from $1/r_2$

The given values are related to copolymerization with styrene [18, 38].

T246	0.55
T345	0.59
T245	0.77
T234	1.0
D24	1.66
Styrene	1.0

Classification of Methyl Acenaphtylenes from $1/r_2$

The given values are related to copolymerization with styrene.

Methyl-1	9
Methyl-5	5
Methyl-3	4
Acenaphthylene	4
Styrene	1

It has been generally difficult to obtain values of reactivity for the methoxy styrenes toward the cation styrene because copolymerization between these monomers does not occur very often. For example, the copolymerization of styrene and 2,4-dimethoxy styrene does not yield a true copolymer, but a mixture of both homopolymers. The same result was obtained with the 2,3,4-trimethoxy styrene. For 2,5-dimethoxystyrene—styrene, the reactivity ratios are $r_1 = 0.75 \pm 0.05$ and $r_2 = 0.30 \pm 0.05$.

Another part of this work was concerned with the examination of complexes between groups on the monomer and the Lewis acids used as initiators. The most interesting result was obtained with 5-methoxyindene [17]: When BF_3 or $TiCl_4$ was the initiator, there was no polymerization below -60°C, but above this limit, the yield was always 100%.

To study this phenomenon, several NMR spectra were registered at -50°C: 1) 5-methoxyindene in CH_2Cl_2, 2) BF_3 in CH_2Cl_2, and 3) 5-methoxyindene/BF_3 in CH_2Cl_2. The chemical shifts observed for the monomer alone in CH_2Cl_2 and for the monomer in CH_2Cl_2 saturated with BF_3 are reported in Table 12. These results are discussed in the section on Discussions and Conclusions.

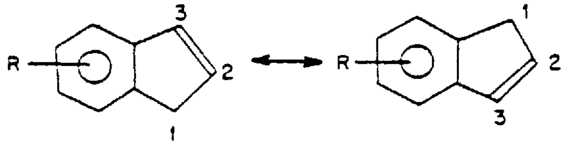
TABLE 12. NMR Spectra for Methoxy Styrene Alone (I) or with BF_3 added (II)[a]

Protons	1	2	4	6	7	OCH_3
I	3.30	6.35	6.95	6.70	7.35	3.75
II	3.30	6.70	7.30	7.05	7.50	4.20

[a] CH_2Cl_2 as solvent and tetramethyl silane as the internal standard.

DISCUSSIONS AND CONCLUSIONS

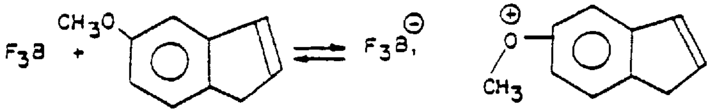
For methyl indenes, comparison of theoretical results (Table 1) and experimental results shows that there is a quite good agreement, the only exception being the 5,7-dimethylindene where the difference between the two determinations is rather large. Theoretically it should be less reactive than indene, but it was experimentally shown that its reactivity is very high and comparable with 4,6-dimethyl or 4,5,6,7-tetramethylindene. It has also been shown that isomerization of the indene-ring often occurs [22]:



After isomerization, an exchange occurs between positions 4 and 7, 5 and 6, and 7 and 4.

The IR spectra of the supposed poly(5,7-dimethylindene) and of poly (5,6-dimethylindene) are quite similar. Consequently, before the addition of this monomer to the end-cation of the growing chain, the monomer should be isomerized into 4,6-dimethylindene. Thus, when the reactivity of 5,7-dimethylindene is determined, it represents the reactivity of 4,6-dimethylindene.

With methoxyindenes, an examination of the theoretical, experimental, and NMR spectroscopy results is necessary. It was shown earlier, that there is a "floor temperature" below which polymerization does not occur. Above this temperature the NMR spectra cannot be analyzed. A proposed structure of the complex is:



The complex ion between BF_3 and the methoxy group does not prevent the association of other BF_3 molecules with the indene ring (π complex, for example). The results reported in Table 12 completely agree with this hypothesis since all peaks are shifted toward the acid part of the spectra (higher chemical shifts).

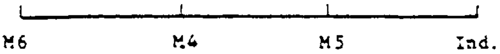
The nearer the proton is to an oxygen atom, the greater the magnitude of chemical shift change is. The larger change is, of course, observed with protons of the methoxy group.

In summary, below a given temperature it must be concluded that the nonpolymerization is probably due to the complex formation between the Lewis' acid and the monomer. However, two assumptions are possible to explain the polymerization which occurs at higher temperatures:

1) As soon as the temperature is above the "floor value," the dissociation of the complex allows an immediate polymerization of the monomer.

2) Above a certain temperature, the complexed monomer is able to polymerize.

The first explanation is the most probable because at a temperature of -50°C, there is an induction period when $TiCl_4$ is the initiator. The quantity of free monomer equilibrated with the complex is certainly very small and the dissociation very slow. But as soon as the reaction starts, the resulting rise in temperature increases the dissociation rate. The experimental and theoretical results are interesting to compare. The experimental reactivities are reported on the following scale figure:



The most reactive monomer toward the styrenic cation is 6-methoxyindene, the reactivity of which is 10 times higher than the styrene reactivity.

. It was shown earlier, that the second set of parameters ($\delta_X = 1$, $\eta_X = 0.8$) gave values of superdelocalizability for the oxygen atom that were not consistent with polymerization. On the other hand, the first set of parameters ($\delta_X = 2$, $\eta_{C-X} = 0.8$) gave smaller values for delocalizabilities on oxygen than on Carbon 2 and consequently were consistent with polymerization and also were sufficiently high to permit the formation of a complex under suitable conditions.

Moreover, this set of parameters has to confer a higher stabilization energy on 6-methoxyindene than on 4,5,6,7-tetramethylindene, since the experimental reactivity of 6-methoxyindene is 10 times higher than for indene. In addition, the reactivity of 4,5,6,7-tetramethylindene is only 7.5 times higher. (However, it has been noted that the first comparison is related to the styrenic cation and the second to the indene cation.)

With the set of parameters $\delta_X = 2$ and $\eta_{C-X} = 0.8$, the same value of $(\Delta E)_r^s$, (0.961), is obtained for 6-methoxyindene and 4,5,6,7-tetramethylindene. Consequently, $\delta_X = 1.8$ and $\eta_{C-X} = 0.8$ is in better accord with the behavior of 5-methoxyindene. After several runs, $\delta_X = 1.6$ was chosen.

In contrast to the results for methylindenes, disagreements between experimental and theoretical reactivities appear for methoxyindenes. Thus the experimental value of 5-methoxyindene is higher than expected. Two hypotheses can be offered:

1) The monomer is released from the complex in an activated form and is consequently of a higher reactivity.

2) The monomer is isomerized into 6-methoxyindene which is obviously more reactive. The isomerization of derivatives 5 and 6 is commonly observed.

The ability of only 5-methoxyindene to yield a complex with Lewis acids is somewhat surprising. Strictly speaking, it is not possible to state that there is no complexion with other monomers when the temperature is low enough. Moreover, the complex formation is easier to explain for 5-methoxyindene than for the other monomers studied. Superdelocalizability values on oxygen and Carbon 2 are given for four monomethoxyindenes in Table 13.

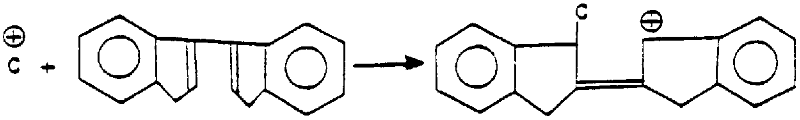
TABLE 13. Values of Superdelocalizabilities on Oxygen and Carbon-2 for Methoxy-4, Methoxy-5, Methoxy-6, and Methoxy-7 Indenes

	Monomer			
Atom	MeO-4	MeO-5	MeO-6	MeO-7
Oxygen	1.181	1.169	1.180	1.156
Carbon 2	1.360	1.250	1.357	1.256
Δ_{O-2}[a]	0.179	0.081	0.177	0.100

[a] ΔO-2 is the difference between the superdelocalizabilities on O and Carbon 2.

It is obvious that the smaller ΔO-2 becomes, the more complex formation is facilitated since this reaction and the attack of C_2 by a carbocation are concurrent reactions. Examination of Table 13 clearly shows that complex formation can occur with 5- and 7-methoxyindenes only. Unfortunately, this last monomer could not be synthesized.

For benzindenes, the attack of monomer by a carbocation always occurs on Carbon 2. It is the most convenient position since the resulting cation on benzindenes is conjugated with a phenyl ring. It may be possible to conclude the same thing for 4,4'-, 5,5'-, 6,6'-, 7,7'-bisindenyls. The most unfavorable case seems to be for the 4,4'-bisindenyl. The situation of 2,2'- and 3,3'-bisindenyls is peculiar; an examination of superdelocalizability values indicates that the attack should be possible only on C_3 for the 3,3'-bisindenyl and on C_2 for 2,2'-bisindenyl and would result in a concerted polymerization between the two π bonds.



This assumption has been partly sustained through the examination of the fluorescence spectra of poly(3,3'-bisindenyl). However, it is difficult to reach a conclusion with certainty because an important part of the fluorescence of this polymer is probably due to the end group.

The examination of values of $(\Delta E)_r^s$ or L_r (Table 2) for

2,2'- and 3,3'-bisindenyl for an attack in position 2 or 3 shows that the ability for these monomers to polymerize is very similar (the reactivity is perhaps slightly higher for the 3,3'-bisindenyl).

The results obtained with trimethylstyrenes seem somewhat strange on first examination. The experimental classification (with $1/r_2$) is T246 $\simeq$ T345 $<$ T245 $<$ T234 $<$ D24, and the theoretical classification is T345 $<$ T245 = T234 $\simeq$ D24 $<$ T246. Moreover, polymerization is always possible for the trimethylstyrenes, and the growing chain is not hindered by the steric effect of the methyl group. Thus with 2,4,6-trimethylstyrene polymers, with $[\eta] = 4$ and 5 (100 ml/g) average molecular weights of several millions were obtained.

Examination of the molecular models shows that the presence of one (and certainly two) methyl groups strains the vinyl group out of the plane of the phenyl ring. Hückel's method does not take account of this fact and treats these molecules as if they were planar. This may account for the difference between experimental and theoretical results.

This assumption has been confirmed by the determination of the coupling constants from NMR spectra. If J_{AB} (Hz) represents the coupling constant of hydrogen atoms H_A and H_B of the methylenic group, the results reported in Table 14 are obtained.

Examination of these values confirms that the vinyl group is no longer conjugated with the phenyl ring. This fact is also in agreement with the classification obtained for styrene disubstituted in the ortho position since the coupling constant is very near to the value obtained for ethylene. Nevertheless, there is no good explanation for the discrepancy between experimental and theoretical reactivity observed for styrene.

It was difficult to derive any valuable conclusion for methoxystyrenes since there were too few experimental values. This failure to obtain more values for the reactivity ratios was previously explained in the Experimental Studies section. The values obtained for 2,5-dimethoxy compared well with the accepted values for monomethoxystyrenes and were generally in good agreement with the theoretical

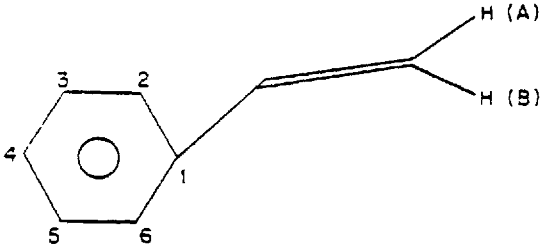


TABLE 14. Values of Coupling Constants J_{AB} for Some Methyl Styrenes

Monomer	J_{AB} (Hz)
Styrene	0.9
Me (3 or 4)	1.0
Me (2)	1.6
DiMe (2,4)	1.5
DiMe (2,5)	1.5
TriMe (2,4,5)	1.5
TriMe (2,3,4)	1.8
DiMe (2,6)	2.1
TriMe (2,4,6)	2.2
Ethylene	2.5

classification. However, it has been shown [42] that the polymerization of these monomers is very often disrupted by the formation of a complex between the growing chain and initiator, and therefore does not go further than a trimerization. (This trimer is complexed by the Lewis acid.)

The results of the acenaphthylene series are very interesting. The classification of methyl acenaphthylenes in regard to their experimental reactivity toward styrenic cation is in complete agreement with their theoretical reactivity. However, for acenaphthylene-styrene, a discrepancy results between experimental and theoretical reactivities. Experimentally, the reactivity of acenaphthylene is four times higher than for styrene, but the stabilization energy obtained for acenaphthylene is smaller than for styrene (0.912). This phenomenon is certainly due to the fact that Hückel's method neglects the ring strain of pentagonal cycle. It is the only discrepancy between the two systems since they are both wholly conjugated and there is no choice of parameter. But, as early as 1951, Pullman [43] pointed out that Hückel's calculations for acenaphthylene gave a value obviously too high for the polar moment compared with the experimental value. This paper has also shown that the discrepancy is due to the failure of Hückel's method to express the ring strain effect.

In addition, calculations with Pople's method (CNDO II) were made and the stabilization energy involved in the attack of acenaphthylene and styrene by the styryl cation was determined. The values obtained are, with the same units, 6.756 for styrene and 6.993 for acenaphthylene. Thus, with Pople's method which takes into account the geometry of the molecule, the discrepancy between theoretical and experimental results disappears. This fact seems to prove the importance of ring strain in acenaphthylene polymerization.

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