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**Structure and Reactivity of Vinyl Aromatic Monomers
in Coordinated Anionic Polymerisation and Copolymerisation**

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The stereospecific polymerisation of vinyl hydrocarbons to isotactic polymers has been extended, since the beginning of our researches, to the field of vinyl aromatic monomers¹).

In the course of a systematic research work, about thirty vinyl aromatic monomers have been prepared in our laboratory²) and polymerized with catalysts from Al alkyls and Ti halides, following reaction conditions selected from the deeper study of the styrene isotactic polymerisation^{3,4}).

We recently described⁵) the properties of the polymers obtained and briefly discussed the influence of the structure of the monomers on their reactivity and on the physical properties of the corresponding polymers. We report here in some detail the results on the relative reactivities of vinyl aromatic monomers in stereospecific polymerisation and copolymerisation.

The results, especially those concerning substituted styrenes, can be interpreted in terms of polar and steric effects of the substituents; hence, the possibility of reaching a clearer understanding of the mechanism of this unusual polymerisation.

An extensive experimental investigation showed us⁶) that in stereospecific polymerisation with the above mentioned catalytic systems all

¹) G. NATTA, *Atti Accad. naz. Lincei, Mem.* (8) 4 (1955) 61; G. NATTA, P. PINO, P. CORRADINI, F. DANUSSO, E. MANTICA, G. MAZZANTI, and G. MORAGLIO, *J. Amer. chem. Soc.* 77 (1955) 1708.

²) D. SIANESI, in press on *Gazz. chim. Ital.*

³) G. NATTA, F. DANUSSO, and I. PASQUON, *Coll. Czechoslov. chem. Commun.* 22 (1957) 191.

⁴) G. NATTA and F. DANUSSO, *Chim. et Ind.* 40 (1958) 445; F. DANUSSO, D. SIANESI, and B. CALCAGNO, *Chim. et Ind.* 40 (1958) 450, 628, 909; 41 (1959) 13.

⁵) G. NATTA, F. DANUSSO, and D. SIANESI, *Makromolekulare Chem.* 28 (1958) 253.

⁶) D. SIANESI, G. NATTA, and F. DANUSSO, Communication presented at the VIII Congresso Naz. della Società Chimica Italiana, Torino, May 26th, 1958; D. SIANESI, M. RAMPICHINI, and F. DANUSSO, *Chim. et Ind.* 41 (1959) 287; other papers to be published shortly in *Chim. et Ind.*

vinyl aromatic monomers, which were polymerized, follow the kinetic laws which we have found to hold in the case of unsubstituted styrene⁴).

Although we have to deal with heterogeneous catalytic systems, acting with an ionic mechanism, the polymerisation can be experimentally carried out in such conditions as to assume constant or regular features, and studied with relatively simple, isothermal methods.

Depending on the nature of the catalytic reagents and the conditions in which they are brought in contact, the catalyst may be either stable or unstable during the polymerisation. But even in the latter case it is possible to isolate and study the factors influencing the essential polymerisation reaction, independently from the other factors determining the overall process. It is thus possible to obtain reliable results, which offer the possibility of reaching valid theoretical conclusions³).

The polymerisation reaction is, per se, a first order reaction with regard to both the monomer and the catalyst, having an activation energy of the order of 10,000–14,000 cal mol⁻¹.

In order to establish a scale of reactivity of differently substituted monomers in the overall polymerisation process, we have determined the *relative reactivity* a of each monomer (in its homopolymerisation).

The relative reactivity a of each monomer was defined as the ratio between its overall rate constant k_{mon} and the correspondent constant of the styrene k_{styr} , at a same temperature:

$$a = \frac{k_{\text{mon}}}{k_{\text{styr}}} \quad (1)$$

Being in general:

$$v = - \frac{dm}{dt} = k \cdot c \cdot m \quad (2)$$

we have in some instances determined a by dilatometric measurements⁴) as the ratio between initial polymerisation rates in separate equivalent polymerisations of each of the two monomers; in other cases a has been calculated from conversion data at a same reaction time, by the equation (derived from (2)):

$$a = \frac{\log (1 - \eta_{\text{mon}})}{\log (1 - \eta_{\text{styr}})} \quad (3)$$

where η_{mon} and η_{styr} are the conversion yields of the two monomers, in the same experimental conditions. The a values of several monomers are listed in table II.

On the other hand, beside the knowledge of the reactivities toward the overall process, it is of fundamental interest to determine the relative reactivities of the monomers in the elementary process of chain growth.

By polymerizing a mixture of monomers, we have obtained products whose copolymeric nature has been proved by us, also on the basis of X-ray and infrared-ray examinations. Thus we have been able to calculate conventional *reactivity ratios* r_1 and r_2 for several monomers, copolymerized with styrene. In order to analyse the products easily and to check their homogeneity, labelled styrene was used as co-monomer.

In table I the reactivity ratios of some monomeric systems are reported. The corresponding composition curves have a regular shape, which is typical of an ideal copolymerisation. The ideal character of the copolymerisation is also evidenced by the $r_1 \cdot r_2$ values, which are very close to unity, and also confirmed by particular infrared studies, showing in the cases so far examined a random structure of the copolymers.

Table I. Reactivity ratios of some substituted styrenes at 40°C.
(monomer 1 = styrene)

Monomer 2	r_1	r_2	$r_1 \cdot r_2$
p-methylstyrene	0.82 (± 0.1)	1.15 (± 0.05)	0.95
m-methylstyrene	2.0 (± 0.2)	0.5 (± 0.1)	1.0
p-ethylstyrene	1.0 (± 0.2)	1.0 (± 0.2)	1.0
p-fluorostyrene	1.5 (± 0.2)	0.7 (± 0.1)	1.0
p-chlorostyrene	2.2 (± 0.2)	0.5 (± 0.1)	1.1
p-bromostyrene	1.7 (± 0.3)	0.5 (± 0.2)	0.85

A particular interesting result is that the values of the reactivity ratio r_2 in copolymerisation are practically identical to the values of relative reactivity a in homopolymerisation. In table II the r_2 values for several monomers (all referred to styrene) are compared with those of a .

It should be noted that the found a and r_2 (or r_1) values of each monomer are not substantially different, even when they are determined using rather different catalytic systems, having different activity (e.g.: $\text{TiCl}_4 + \text{Al}(\text{i.C}_4\text{H}_9)_3$; $\text{TiCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$; $\text{TiCl}_3 + \text{Be}(\text{C}_2\text{H}_5)_2$). They actually depend only on the polymerisation temperature.

An ideal character of the copolymerisation has already been admitted for copolymerisation following an ionic mechanism⁷⁾. On the other hand, the equality $a = r_2$ has never been so clearly observed previously.

⁷⁾ Y. LANDLER, J. Polymer Sci. 8 (1952) 64.

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Table II. Relative reactivities in polymerisation and reactivity ratios in copolymerisation of some substituted styrenes with regard to the styrene at 60°C.

Substituent in the styrene	a a)	r_2 b)
H	1	1
o-methyl	0.10	0.13
m-methyl	0.43	0.48
p-methyl	1.2	1.16
2.4-dimethyl	(0.08)	0.14
2.5-dimethyl	(0.03)	(0.03)
3.4-dimethyl	0.48	—
3.5-dimethyl	0.23	—
2.4.6-trimethyl	0	0
p-ethyl	1.1	1.05
p-isopropyl	0.49	—
p-cyclohexyl	0.50	0.58
o-fluoro	0.20	0.18
m-fluoro	0.50	0.47
p-fluoro	0.74	0.72
o-chloro	0	—
m-chloro	0.40	0.43
p-chloro	0.45	0.49
p-bromo	0.50	0.48 ^{d)}
p-methoxy	2–3 ^{c)}	1.6
β -C ₄ H ₄ (2-vinylnaphthalene)	0.67	—

a) Calculated from experimental values of polymerisation rate or conversion.

b) Calculated for ideal case from experimental composition of a copolymer, prepared by low conversion 1:1 copolymerisation.

c) Estimated value: the monomer interacts with the catalyst.

d) at 40°C.

In fact, in a conventional ionic polymerisation, with a chain mechanism, the overall rate is in general thought to be prevalently determined by the initiation rate⁸⁾, as well as being influenced by a termination rate, and is not representative of the value of the propagation rate. This is, on the contrary, the completely determining factor of the reactivity ratios in copolymerisation.

The ideality of our copolymerisation and the identity between a and r_2 , show that in our polymerisation conditions:

a) the relative tendency of a monomer to enter in a polymer chain depends only on the structure of the entering monomer, but not on the nature of the terminal unit of the growing macroion.

⁸⁾ T. YONEZAWA, T. HIGASHIMURA, K. KATAGIRI, K. HAYASHI, S. OKAMURA, and K. FUKUI, *J. Polymer Sci.* **26** (1957) 311.

- b) in classical terms (of conventional chain reactions) no differentiation is detectable between an initiation and a propagation step;
- c) in the same terms, and also according to kinetic results, a true termination step was never evidenced.

In other words our polymerisation apparently proceeds, from the point of view of the monomer consumption, through a single type of step. We have, therefore, practically to deal with a stepwise addition process, in which the ultimate length of the macromolecules of the polymer may be determined by some elementary reactions, already recognized⁹⁾, having the features of transfer reactions.

In order to understand the mechanism of the fundamental addition reaction better, it is of great significance to examine the relationship between structure and reactivity for the monomers studied.

For this purpose, the data of table II were arranged following a HAMMETT plot (excluding, of course, all ortho substituted monomers)⁹⁾. Fig. 1 shows that, for halogen or p-n-alkyl substituted styrenes and for some other monomers, a linear relation may be considered to hold between $\log a$, or $\log r_2$, and the σ constant values corresponding to each type of substituent in the phenyl nucleus.

A few other monomers (p-isopropylstyrene and m-methyl substituted styrenes) on the contrary have, a or r_2 values lower than those which would be predicted from the above linear relation.

The behavior of these last monomers could be ascribed to factors of steric hindrance. Even if in the case of simpler reactions steric effects are not normally observed in examinations of meta or para substituted compounds, it is not surprising to find them in a reaction which has a stereospecific character and is promoted by heterogeneous catalysts. An evident confirmation of the importance of steric requirements in our polymerisation is given by the very low reactivity of ortho (and even more of diortho) substituted styrenes, some of which are completely inactive.

The validity of the HAMMETT rule for a significant group of monomers indicates a regular response of the reaction to the electronic configuration of the monomer.

The most interesting result is, however, the negative slope of the straight line of Fig. 1 ($\rho = \sim -1.0$), indicating that the reaction is favoured in the case of monomers having an electron releasing substituent.

⁹⁾ L. P. HAMMETT, Physical Organic Chemistry, McGraw-Hill, New York 1940, pp. 184 to 207.

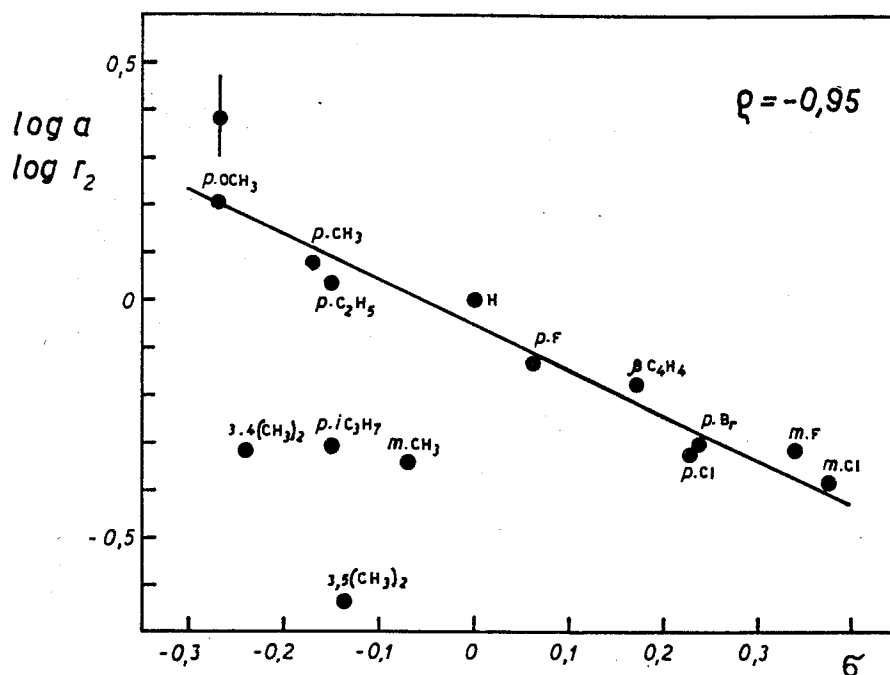


Fig. 1. Mean values of relative reactivity and reactivity ratio of Table II, ordered following the Hammett plot

The greater the electronic density on the double bond, the more reactive the monomer is, as if an electrophilic attack on the double bond was kinetically determinant.

Considering only r_2 values, this might at first sight appear as a typical feature of the cationic polymerisation¹⁰), in which a positive growing ion attacks the monomeric double bond.

However, it should first be noted that in a conventional cationic polymerisation, so far known:

- ideal copolymerisation may sometimes take place, but the equality $a = r_2$ has never been till now recognized to hold;
- following our further data obtained with conventional cationic catalysts, r_2 values of the same meta or para substituted monomers above examined all fit on a straight line in a HAMMETT plot, while in Fig. 1 exceptions in defect were observed;
- ortho substituted monomers (and α -substituted, as α -methylstyrene) have high reactivities, while in our polymerisation they are completely inactive or show very low reactivities.

¹⁰) See for instance: G. C. OVERBERGER, L. H. AROND, D. TANNER, J. TAYLOR, and T. ALFREY, J. Amer. chem. Soc. 74 (1952) 4848.

Furthermore, many arguments were found and evidenced in some of our preceding papers (see for ex. ^{11, 12, 13}) strongly supporting that the polymeric chain must be built up by addition of polarized $\overset{(-)}{\text{CH}_2}-\overset{(+)}{\text{CHR}}$ monomeric units to the activated $\overset{(-)}{\text{CH}_2}$ - end group of a growing chain. Some of these may be summarized as follows:

- a) the nature of certain bonds in the catalytic complexes, in which carbon atoms act as a ligand and are connected to highly electropositive metal atoms;
- b) the close analogy to simpler addition reactions of olefins to similar metallorganic compounds or complexes;
- c) the value of the activation energy of the polymerisation;
- d) the presence in the polymers, as end groups, of the alkyl or aryl groups which were initially bound as ligands to the metallorganic catalytic complexes;
- e) the presence of vinylidenic end groups in the macromolecules of aliphatic polyolefins, as a result of a H^- transfer from the $-\text{CHR}-$ group of the terminal monomeric unit of the growing chain to the catalyst or to an entering monomer molecule;
- f) the presence of radioactive carbon atoms in the polymers, when labeled CO_2 is used to stop the polymerisation¹⁷).

The fact that the stereospecific polymerisation of vinyl aromatic monomers is intrinsically of the anionic type (with a negative growing ion), but does not respond to the polarity of the substituents according to a conventional anionic polymerisation (favoured by electron attracting substituents) may appear to be quite peculiar. But it can find an interpretation in the mechanism already proposed for a "coordinated anionic polymerisation"¹²), in which a fundamental role is thought to be played by a previous step of coordination of the monomer to the transition metal of the catalyst.

¹¹) G. NATTA, P. PINO, E. MANTICA, F. DANUSSO, G. MAZZANTI, and M. PERALDO, *Chim. et Ind.* **38** (1956) 124.

¹²) G. NATTA, *Experientia Suppl.* **7** (1957) 21; G. NATTA, *Ricerca sci. Suppl.* **28** (1958).

¹³) G. NATTA, P. PINO, G. MAZZANTI, and U. GIANNINI, *J. Amer. chem. Soc.* **79** (1957) 2975; *Ricerca sci. Suppl.* **28** (1958).

¹⁴) See for instance: M. SZWARC, M. LEVY, and R. MILKOVICH, *J. Amer. chem. Soc.* **78** (1956) 2656.

¹⁵) G. J. M. VAN DER KERK, J. G. NOLTES, and J. G. A. LUIJTEN, *J. appl. Chem.* **7** (1957) 356.

¹⁶) G. NATTA, P. PINO, G. MAZZANTI, P. LONGI, and F. BERNARDINI, *J. Amer. chem. Soc.*, in press.

¹⁷) Data to be published shortly.

According to our experimental results, as well as to evidences on the structure of some catalytic complexes¹³⁾ and to results on the stereospecific polymerisation of α -olefins, the mechanism of the single addition step of our polymerisation may be interpreted as follows.

The methylenic end of the alkyl groups, contained in the catalytic complex, or of the growing polymeric chain, is bound to the electron deficient catalytic complex, the bond having a partially ionic character, at least in its activated state. Thus, the negative terminal of the chain can be thought of as bound to the metals of the complex, likely in a closer manner to the more electropositive one (e.g. Al).

When a monomer molecule approaches the catalytic centre, addition may occur following two fundamental stages.

1. According to the common rules of the heterogeneous catalysis, a chemisorption of the monomer should take place to a region of the surface of the catalyst in which a transition metal atom acts as a coordinating centre. The coordination must be accompanied or immediately followed by polarisation of the vinyl double bond, due to local field conditions.

As actual result of this stage, a positive charge must be localized on the α carbon atom of the vinyl group *).

2. The positive carbon atom of the monomeric unit turns toward the negative terminal of the growing chain. Then, neutralisation and covalent bond formation take place, followed by approaching of the new chain end to the more electropositive metal atom, so that initial situation is restored.

The experimentally observed favourable effect of electron releasing substituents on the reactivity in the case of vinyl aromatic monomers, would depend on the controlling nature of the first stage, in which the vinyl group acts as a nucleophilic reagent favouring the coordination of the monomer to the more electron deficient part of the complex.

*) It is known¹⁴⁾ that as a consequence of a nucleophilic attack on the styrene in the presence of the cation of a monovalent, strongly electropositive metal (e.g. Na, Li), the negative charge is localized on the α -carbon atom. In the formation of phenylethylic metallorganic compounds with a polyvalent, less electropositive metal (e.g. Sn), the metal is bound to the methylenic group in β -position¹⁵⁾. In the case of the formation of phenylethylic aluminum compounds (by reacting styrene with triisobutyl aluminum) an equilibrium composition of α - and β -substituted isomers is obtained, displaced toward the latter isomer¹⁶⁾. It is therefore possible to foresee that, by coordinating of a styrene molecule to a complex containing Ti and Al, a polarization of the double bond must occur, as an electron displacement toward the β -position.

In a conventional anionic polymerisation (e.g. catalyzed by sodium alkyls), on the contrary, as a consequence of a previous attack of the growing carbanion, a negative charge would be stabilized on the α carbon atom and an increase of electron density on the vinylic double bond would be unfavourable to the addition reaction.

As a consequence also of the outlined mechanism, in our polymerisation the coordination stage effected by electrodeficient bimetallic complexes may further imply spatial requirements and arrangements, which may be at the same time the origin of the stereospecificity, but also the reason of the lower reactivity observed with sterically hindered monomers.

It is interesting to note that, in the case of stereospecific polymerisation of α -olefins, the reactivity of the monomers appears to decrease in the order: ethylene, propene, butene, 3-methyl butene, 3.3-dimethyl butene. Considering only the polar effect of the substituents, this behavior would be reversed with respect to that observed with vinyl aromatic monomers, but typical of a normal anionic polymerisation. This would mean that for the α -olefins the formation of a π -complex, followed by polarization of the double bond and by a nucleophilic, kinetically controlling attack of the negative growing anion, could be envisaged. However, steric effects must also play an important role in the establishment of the above reactivity scale.