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Stereospecific Polymerization and Isotactic Polymers of Vinyl Aromatic Monomers

By Giulio Natta, Ferdinando Danusso, and Dario Sianesi

(Eingegangen am 3. November 1958)

During the last years, considerable research work was carried on at our institute on the stereospecific polymerization of mono- and polynuclear aromatic vinyl monomers, particularly of nuclear substituted styrenes.

As soon as we have obtained isotactic crystallizable, high melting polymers of styrene¹), we considered with great interest the possibility of obtaining stereo-ordered polymers from other aromatic monomers, by employing typical stereospecific catalytic systems, and of studying their physical and technological properties.

Furthermore, it appeared at the same time to be very promising to carry out a systematic research, in order to determine the relationship between the monomer structure or the kind of substitution and the monomer reactivity in an anionic coordinated polymerization and, eventually, the stereospecifity of the catalytic system.

We resume in the present paper some of our most interesting results²).

By studying the behavior of many arylsubstituted vinyl monomers, we found that stereospecific polymerization can be applied to almost the whole class of such monomers, excepting, of course, the monomers containing bonds or groups reacting with the component of the catalyst (e. g. those containing active hydrogen atoms, or groups containing atoms with lone electron pairs: O, S, N, ..).

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¹) G. Natta, Atti Accad. Naz. Lincei, Mem. **8** (1955) 4; G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, J. Amer. chem. Soc. **77** (1955) 1708.

²) See for ex.: D. Sianesi, G. Natta, and F. Danusso, communication presented at the VIII. Congresso Nazionale della Soc. Chimica Italiana, Torino, May 26th, 1958; other papers to be published in "Chimica e Industria".

³) F. Danusso and D. Sianesi, Chim. e Ind. [Milano] **40** (1958) 450; F. Danusso, D. Sianesi and B. Calcagno, ibid. **40** (1958) 628; F. Danusso and D. Sianesi, ibid. **40** (1958) 909.

With polymerizable aromatic monomers the features of the polymerization appeared to correspond remarkably to those we had observed[3]) in the case of styrene. This enabled us to obtain by polymerization practically only high polymers having a linear and ordered structure, under conditions leading uniquely to a coördinated anionic process, using catalysts prepared from $TiCl_4$ or $TiCl_3$ and organo-aluminum compounds. In this way, it was possible to avoid all other cationic or radical polymerization mechanisms, towards which many of these monomers are extremely sensitive. The polymers obtained consisted essentially, therefore, of one fraction, that could not be further separated with solvents into fractions having different structural order.

Depending on the structure of the monomer, these polymers are in some cases crystallizable to an high or medium degree of crystallinity, while in other cases they are not crystallizable (at least by conventional annealing).

It is interesting to note that the stereospecific polymerization of vinyl aromatic monomers can be highly efficient also with catalysts which, with aliphatic α-olefins, are only little or moderately stereospecific. Whereas, with aliphatic α-olefins the catalyst from violet, crystalline $TiCl_3$ are more stereospecific than those from $TiCl_4$, in the case of vinyl aromatic monomers the difference is not so evident.

In table 1 the monomer structure and the main properties of the polymers obtained by stereospecific catalysis are reported. In the last column, data of yield of polymers obtained under the same experimental conditions, are also compared; for this comparison, it was considered preferable to report the result obtained with a catalyst from $TiCl_4$. With this catalyst, experimental data are in general well reproducible, not being dependent on the physical state or particle fineness of a solid titanium compound, such as $TiCl_3$.

The data of the table 1 show that the characteristics of crystallizability of the polymers listed are markedly dependent on the type and the site of substitution of the corresponding monomer.

It is to be noted that such dependency does not seem to be related to the polar character of the substituent, i. e. to the modifications that the substituent may cause to the electronic configuration of the monomer and more particularly to the polarizability of the vinyl double bond. It appears, on the contrary, strictly related to the size, the site and the number of substituents, that is, to steric reasons.

Thus, polymers of para substituted styrenes are not crystallizable at all, when the size of the substituent is not very small. The poly(p-fluorostyrene) is, in fact, the only crystalline para substituted polymer we have been able to obtain, evidently because of the small difference between the VAN DER WAALS radii of an hydrogen and a fluorine atom.

Ortho substituted monomers, if polymerizable, give, on the contrary, polymers which are easily crystallizable. The same ability is shown by polymers of di-substituted (e. g. dimethyl) styrenes, even if para position is involved.

Crystalline polymers, listed in the table, have generally a very high crystal melting temperature and, some of these, higher than the decomposition temperature. Crystallinity degrees are, in some cases, equal to, but in other cases higher than, that which can be reached with isotactic polystyrene. Crystallization rates, at temperatures above glass transition, can be very high, as in the case of ortho-substituted polystyrenes. Thus, contrary to the behavior of polystyrene, with these polymers high crystallinities are reached in few seconds at a temperature some ten degrees below the melting temperature.

A preliminary examination of the structures of the crystalline polymers[4]) enabled us to conclude that they are formed by isotactic and, consequently, spiralized macromolecules. Identity period along the c-axis of the crystals (i. e. helix axis) depends on the monomer structure. While in the case of the poly(o-fluorostyrene) the pitch of the helix comprises three monomeric units, as in polystyrene, in the case of the polymers of o-methyl, p-fluoro, 2-methyl-4-fluorostyrene, and 1-vinylnaphthalene it comprises four monomeric units. For the four polydimethylstyrenes and the poly(m-methylstyrene), a greater number of monomeric units corresponds to the identity period.

These crystallizable isotactic polymers, if examined in the amorphous state, show some small differences in the properties, when compared with correspondent amorphous atactic polymers prepared by conventional non stereospecific, e. g. radical methods.

In a quite similar manner behave the rest of the polymers listed in the table: although they are non crystallizable, they show certain differences in many physical properties, when compared with correspondent atactic radical polymers.

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[4]) G. NATTA, P. CORRADINI, and I. W. BASSI, communications presented at the VIII. Congresso Nazionale della Soc. Chimica Ital., Torino, 1958.

In some instances, these differences, apparently very remarkable, have to be, of course, partly attributed to the considerable differences in the molecular weights between the two types of polymers. In the polymerization conditions, used in this work, the stereospecific process leads, in fact, to considerably high molecular weights, as is roughly shown by intrinsic viscosity data reported in table 1. Such molecular weights are generally of the order of magnitude of 10^6, whereas it is very difficult, in some instances impossible, to reach so high molecular weights by using free radical or cationic polymerization methods.

In many instances, however, the difference in the properties, such as differences observed in I.R. absorption spectra, must certainly be attributed to a difference in the steric regularity of the macromolecules of the two types of polymers.

Thus, on the basis of various results and conclusions on the formation mechanism, and on the properties of these non-crystallizable polymers, we believe they are essentially constituted by macromolecules, not only completely linear, but also regular in steric configuration of the units, like the typical isotactic polymers. Consequently, in these polymers, the physical process of crystallization is remarkably slowed or completely avoided to occur by particular steric hindrances of the substituents.

Following, for instance, general rules holding in crystallization of linear high polymers, crystallization cannot be possible in all cases where an ordered structure should imply a bad spatial filling, due to the size and positions of the side chains, in such a way to lead to a density in the crystal phase smaller than that of the amorphous phase.

Steric hindrances may take place with regard not only to the spiralization of a single macromolecule, which is peculiar for isotactic polymers, but also to the packing of several already spiralized macromolecules in a crystal lattice.

The nature of the substituent affects not only the crystallizability and other physical properties of the polymers, but also considerably the reactivity of the monomers in the coordinated anionic polymerization. Conversion data reported for each monomer in the table, all obtained in the same experimental conditions, may be an approximate measure of such reactivity.

A deeper study is, however, being carried out on this matter based on measurements of initial polymerization rates and aiming to the knowledge of quantitative relations between the monomer structure, or particularly the site and the type of substitution in the styrene nucleus, and the monomer reactivity in coordinated polymerization. It may be, however, since now understood that this polymerization process is particularly sensitive to the presence of rather hindering substituents on the nucleus in the proximity of the vinyl group.

An ortho substitution in the styrene leads in any case to a considerable decrease in the reactivity of the monomer, which in some cases can also be practically inactive with regard to the catalysts employed. This last behavior seems to be a general one of di-ortho substituted styrenes.

Reactivities of meta or para substituted styrenes, are generally markedly dependent on the polar character of the substituents, save the case of styrenes substituted with groups having considerable steric requirements, for which one may observe irregular decreases in reactivity, which are to be ascribed to steric hindrance phenomena.

In particular, the values of polymerization rates, referred to that of the styrene, of several meta and para substituted styrenes fit the HAMMET equation(5). The slope of the straight line, which is a measure of the susceptibility of the reaction to polar substituents, is negative. This clearly shows that, apart from steric inhibition effects, the reactivity of the monomer undergoes in a favourable way the presence of electron releasing substituents, what could already be deduced from the conversion data reported in the table.

Such a result is not in keeping with what one would expect from a normal anionic polymerization; on the contrary, it may be in a good agreement with what was stated earlier(6) on the mechanism of the coordinated anionic polymerization, which implies a coordination step of the carbanion, resulting from the polarisation of the olefinic double bond, to the central strongly electropositive metallic atom of the metallorganic catalytic complex.

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(5) L. P. HAMMET, Physical Organic Chemistry, McGraw-Hill, New York 1940, pp. 184 to 207.

(6) See for ex.: G. NATTA, "The catalytic action of complexes in stereospecific polymerization by means of coordinated anionic catalysis". Ricerca Sci., Suppl. **28** (1958).

Table 1

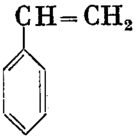
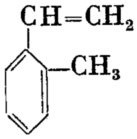
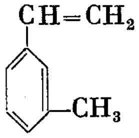
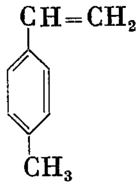
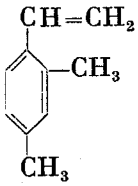
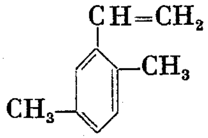
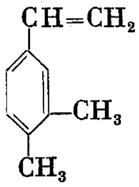
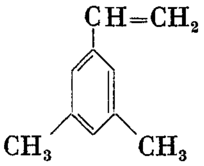
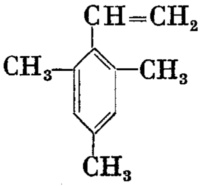
Monomer		Physical state of the polymer a)	Melting temperature (°C.) b)	[η] c)	Conversion yield (%) d)
Styrene		cryst.	240	3.5	43.7
o-Methyl-styrene		cryst.	> 360	n. d. e)	4.6
m-Methyl-styrene		cryst.	215	3.9	22.7
p-Methyl-styrene		am.	–	2.9	49.3
2.4-Dimethyl-styrene		cryst.	310	3.5	4.4
2.5-Dimethyl-styrene		cryst.	330	2.8	1.6
3.4-Dimethyl-styrene		cryst.	240	3.2	21.2
3.5-Dimethyl-styrene		cryst.	290	2.6	12.4
2.4.6-Tri-methylstyrene		....	....	....	0

Table 1

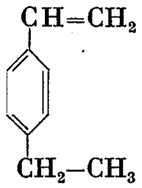
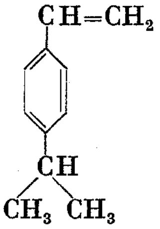
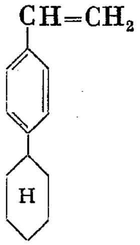
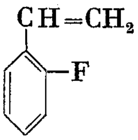
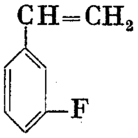
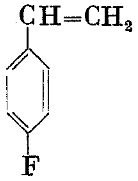
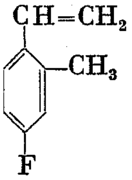
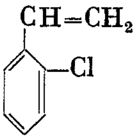
Monomer		Physical state of the polymer a)	Melting temperature (°C.) b)	[η] c)	Conversion yield (%) d)
p-Ethyl-styrene		am.	—	3.5	48.5
p-Isopropyl-styrene		am.	—	3.9	24.2
p-Cyclohexyl-styrene		am.	—	2.5	25.0
o-Fluoro-styrene		cryst.	270	2.3	4.1
m-Fluoro-styrene		am.	—	2.8	24.9
p-Fluoro-styrene		cryst.	265	2.0	39.7
2-Methyl-4-fluorostyrene		cryst.	> 360	n. d. e)	4.3
o-Chloro-styrene		....	....	....	0

Table 1

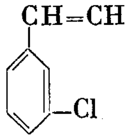
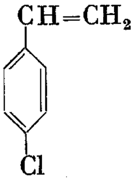
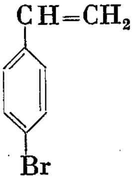
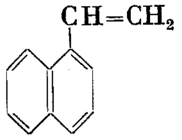
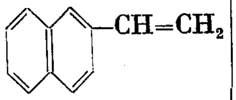
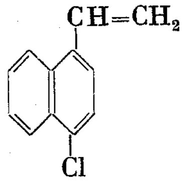
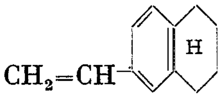
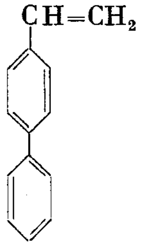
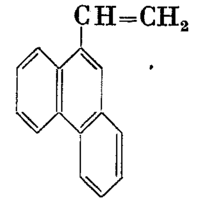
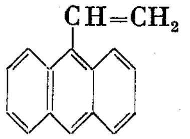
Monomer		Physical state of the polymer a)	Melting temperature (°C.) b)	[η] c)	Conversion yield (%) d)
m-Chloro-styrene		am.	–	3.5	23.2
p-Chloro-styrene		am.	–	2.1	27.8
p-Bromo-styrene		am.	–	1.8	20.1
1-Vinyl-naphthalene		cryst.	~360	2.3	12.9
2-Vinyl-naphthalene		am.	–	3.4	38.9
1-Vinyl-4-chloro-naphthalene		am.	–	1.7	11.2
6-Vinyl-1.2.3.4-tetrahydro-naphthalene		am.	–	2.2	28.3
4-Vinyl-biphenyl		am.	–	0.7	39.2

Table 1

Monomer		Physical state of the polymer a)	Melting temperature (°C.) b)	[η] c)	Conversion yield (%) d)
9-Vinyl-phenanthrene		am.	–	0.7	10.6
9-Vinyl-anthracene		....	....	....	0

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a) Cryst. = crystalline
Am. = amorphous.

The crystalline polymers have been recognized by X-ray and polarizing, hot stage microscope examinations.

In many cases they are in crystalline state since the preparation; sometimes, on the contrary, only after suitable thermal treatments. We have considered as amorphous the polymers, whose X-ray diagrams did not show sharp diffraction peaks also after several attempts of crystallizing them by thermal treatments on the solid polymer at temperatures higher than that of glass transition.

b) Temperature of complete disappearance of the crystallinity, determined by polarizing, hot stage microscope, with heating rate of 1–2 °C./min.

c) Intrinsic viscosity in tetralin at 100 °C., in 100 $cm^3\ g^{-1}$, determined on samples obtained as specified on (d).

d) Polymerization conditions: $2.0 \cdot 10^{-3}$ mols $TiCl_4$; $6.0 \cdot 10^{-3}$ mols $Al(C_2H_5)_3$; $80 \cdot 10^{-3}$ mols monomer; reaction volume: 35 cm^3; solvent: benzene; 7 hours of reaction at 70 °C.

e) Not determined: this polymer was insoluble also in boiling tetralin.