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Progress in the Stereospecific Polymerization

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SUMMARY:

Results of new research work in the field of polymers with an ordered steric structure, obtained by stereospecific polymerization, are reported. Some of the results concern the relationship between steric structure and crystallinity; from these it results that a regular steric structure is a necessary, but not a sufficient condition for the crystallizability of the polymers.

In the isotactic polymers of $CH_2=CHR$ type monomers, the shape and size of the R group not only determine the different conformation of isotactic helices (with a number of monomeric units per pitch varying from 3 to 4) but in some particular cases are responsible for the lack of crystallinity.

It is possible, through chemical processes which modify the shape and size of the R substituent, to obtain crystalline polymers from isotactic, amorphous, not crystallizable polymers.

The crystalline structure of syndiotactic polypropylene is described for the first time and is compared with the structure of other syndiotactic polymers.

Furthermore the structure of crystalline polymers of "di-isotactic type", obtained polymerizing $RCH=CHR_1$ type monomers is discussed; and a nomenclature for the different possible stereoisomers is suggested.

Cases of polymorphism, isomorphism and di-isomorphism in the macromolecular field are examined and a new type of isomorphism among different monomeric units is discussed. Crystalline copolymers of isomorphous monomeric units have a melting point which is intermediate between the ones of the corresponding pure homopolymers.

The effects which influence the steric purity of polymers having an ordered structure are discussed and the influence of steric purity on the physical properties and mainly on the mechanical properties of the polymers (especially for the case of polybutadiene obtained at the Polytechnic of Milan with a percentage of cis 1,4 units higher than 99%) is pointed out.

ZUSAMMENFASSUNG:

Es wird berichtet über neue Untersuchungen an Polymeren mit geordneter sterischer Struktur, die durch stereospezifische Polymerisation erhalten wurden. Einige der Ergebnisse betreffen die Beziehung zwischen sterischer Struktur und Kristallinität; dabei ergibt sich, daß eine regelmäßige sterische Struktur eine notwendige, aber nicht hinreichende Bedingung für die Kristallisationsfähigkeit der Polymeren ist.

Bei den isotaktischen Vinylpolymeren vom Typ $CH_2=CHR$ bestimmen die Form und Größe des Substituenten R nicht nur die verschiedene Konstellation der isotaktischen Helix (mit einer Anzahl von Monomereinheiten, die zwischen 3 und 4 wechseln), sondern sind in einigen besonderen Fällen auch für das Fehlen der Kristallinität verantwortlich.

Es ist möglich, durch chemische Prozesse, welche die Form und Größe des Substituenten R verändern, kristalline Polymere aus isotaktischen amorphen und nicht kristallisierbaren Polymeren zu erhalten.

Es wird zum erstenmal die Kristallstruktur von syndiotaktischem Polypropylen beschrieben und dessen Struktur mit der anderer syndiotaktischer Polymerer verglichen.

Weiterhin wird die Struktur von kristallinen Polymeren vom „diisotaktischen Typ", hergestellt durch Polymerisation von Monomeren des Typs $RCH=CHR_1$, diskutiert und eine Nomenklatur für die verschiedenen möglichen Stereoisomeren vorgeschlagen.

Es werden Fälle von Polymorphie, Isomorphie und Diisomorphie auf dem Hochmolekulargebiet untersucht. Ein neuer Typ von Di-isomorphie zwischen verschiedenen Monomereinheiten wird beschrieben.

Kristalline Copolymere mit isomorphen Monomereneinheiten haben Schmelzpunkte, die zwischen denen der entsprechenden reinen Homopolymeren liegen.

Die Einwirkungen, welche die sterische Reinheit von Polymeren mit geordneter Struktur beeinflussen, werden untersucht. Es wird erörtert, welchen Einfluß die sterische Reinheit auf die physikalischen und besonders die mechanischen Eigenschaften der Polymeren hat; in erster Linie für das Polybutadien, das an der Technischen Hochschule in Mailand mit einem Gehalt von mehr als 99% 1.4-cis-Einheiten erhalten wurde.

Introduction

The stereospecific polymerization processes which had found their first and most important applications in the field of α-olefin and diolefin polymers, have been the object during the last years of further researches with ZIEGLER type catalysts and other different catalytic systems, and it has also been extended to other series of monomers. The results which some years ago had already marked an upheaval in the macromolecular science, have been more and more completed and improved. For instance we succeeded in obtaining polydiolefins of high steric purity and discovered completely new types of crystalline polymers which are remarkably interesting both scientifically and practically.

In this communication I shall refer to some of the researches accomplished at the Polytechnic of Milan, especially those concerning the new types of crystalline polymers and the relations between the steric structure and crystallinity of polymers. We discovered series of new polymers having a regular steric structure such as syndiotactic poly-α-olefins and a completely new group of crystalline macromolecules resulting from the polymerization of monomers with an internal double bond. The discovery of these new polymers for which we proposed the denomination "di-isotactic polymers" does not only call for new problems of terminology, but also gives an impulse to new researches which will lead to a better understanding of the stereospecific polymerization mechanisms.

lack of time, I shall not refer here to other works accomplished in
stitute in the field of stereospecific catalysts. On the relations
n the molecular structure and catalytic activity of some metall-
: complexes of titanium, isolated in their pure state by crystalli-
I have recently referred at the London Congress on the Chemistry
Coordination Compounds[1]) and at the Congress of the International
of Pure and Applied Chemistry in Munich[2]).

Isotacticity and Crystallinity

: of all, I wish to point out the relationship existing between the
structure and crystallinity in the sterically regular polymers.
he basis of a systematic work on stereospecific polymerization and
structure of the obtained polymers, we could demonstrate that
gularity in the chain configuration is for many classes of polymers
cessary condition, but not the sufficient one, for obtaining crystal-
lymers.
different shape and encumbrance of the R substituents in the
ic polymers of $CH_2=CHR$ monomers is the reason of the different
mations assumed by the isotactic helices in the crystals[3]).

Roentgenographic data on some typical isotactic polymers with different chain conformations

Polymer	Helix type *)	Chain axis Å	Unit cell	Space group
opylene	3_1	6.50	Monoclinic a = 6.65Å, b = 20.96Å, β = 99°20′	C2/c
-butene**)	3_1	6.50	Rombohedral a = 17.70Å	R3c or R$\bar{3}$c
yrene	3_1	6.63	Rombohedral a = 21.90Å	R3c or R$\bar{3}$c
-methylhexene-1 .	3_1	6.50		
-methylheptene-1.	3_1	6.40		
-phenylpropene-1 .	3_1	~6.40		
-phenylbutene ...	3_1	6.55		
-methylstyrene ...	4_1	8.10	Tetragonal a = 19.01Å	I4₁cd
-vinyl naphthalene	4_1	8.10	Tetragonal a = 21.20Å	I4₁cd
inyl cyclohexane ..	4_1	6.50	Tetragonal a = 21.76Å	I4₁a
-methylbutene-1..	4_1	6.84		
-methylpentene-1.	7_2	13.85	Tetragonal a = 18.60Å	P$\bar{4}$
-methylhexene-1 .	7_2	14.00	Tetragonal a = 19.64Å	
n-methylstyrene ..	11_3	21.74	Tetragonal a = 19.81Å	

s to be understood that, besides the right-handed X_n helix, also the left-handed
_n helix exists.
dification 1.

Some X-ray data concerning isotactic polymers with different chain
conformations are reported in Table I. All these data, except the values
concerning the elementary unit cell of poly-4-methylpentene-1[4]), are the
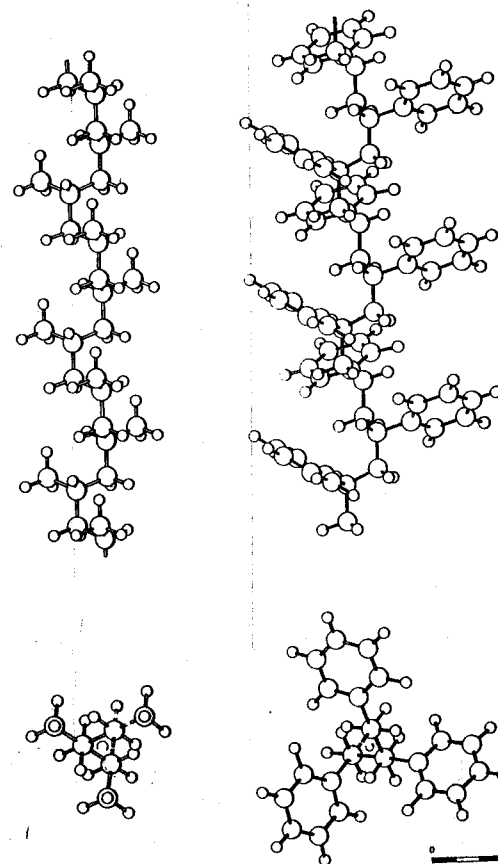result of the examinations performed in our Institute[5]).

Fig. 1. Polymer chain with threefold symmetry
(3_1 polypropylene, 3_1 polystyrene; also hydrogen atoms are drawn)

Fig. 1 shows the models with threefold symmetry of polypropylene and
of polystyrene chains [(AB)₃ according to Bunn[6,7]) with a period of
6.50 and 6.65 Å respectively]; Fig. 2 shows the models with fourfold
symmetry of poly-o-methylstyrene chain [(AB′)₄ with a period of
8.10 Å[7])] and of polyvinyl cyclohexane [(A′B′)₄ with a period of 6.50 Å];
Fig. 3 shows the models of chains, with a more complex symmetry, of
poly-4-methylpentene-1 [(A′B′)₇/₂ with a period of 13.85 Å] and of poly-
m-methylstyrene [(A′B′)₁₁/₃ with a period of 21.74 Å].

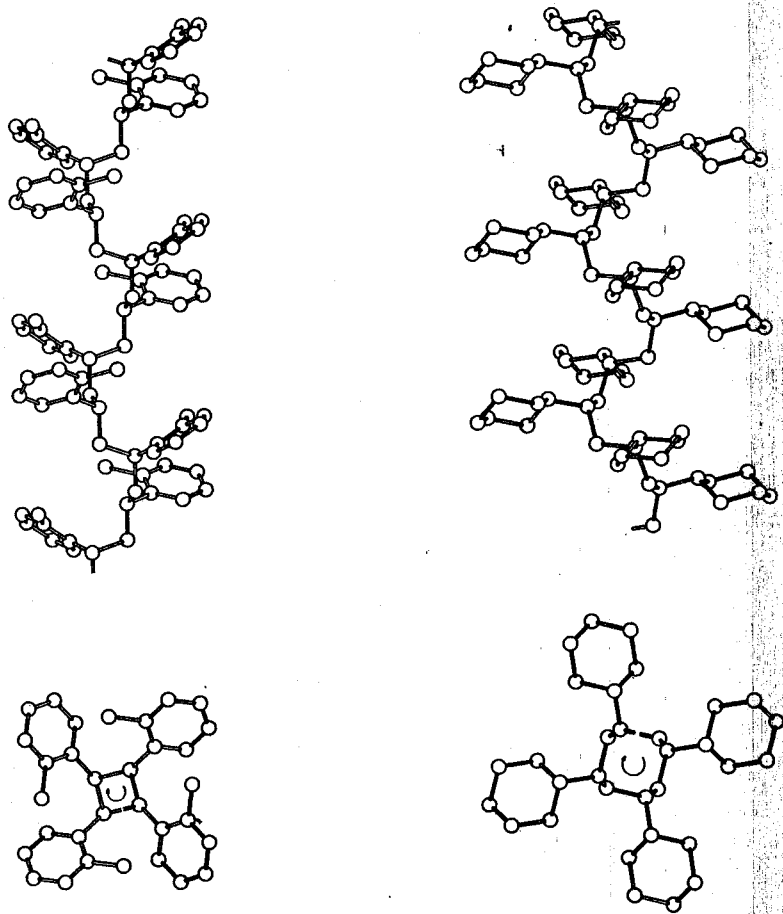The shape and encumbrance of the R side groups in some particular ses may also cause lack of crystallinity.

Fig. 2. Polymer chains with fourfold symmetry
(4₁ poly-o-methylstyrene, 4₁ polyvinyl cyclohexane)

We particularly studied a series of polymers of substituted aromatic onomers; the polymers were obtained using stereospecific catalysts ontaining Ti halides and metallorganic compounds)[8]). The result of ese experiments is that by polymerization of similar monomers on a ereospecific catalyst it is possible to obtain also completely amorphous oducts. Some of these products can crystallize after particular thermal eatments carried out in the presence of small quantities of solvents or elling agents; in other cases the products were not crystallizable by

any means. While for instance isotactic polymers of o- and of m-methylstyrene were crystalline, polymers of p-methylstyrene were amorphous. With regard to monofluorostyrenes, polymers of the o- and p-isomers are crystalline, whereas polymers of the m-isomers are not. Thus polymers of m- and p-chlorostyrene were amorphous. The isotactic polymer of
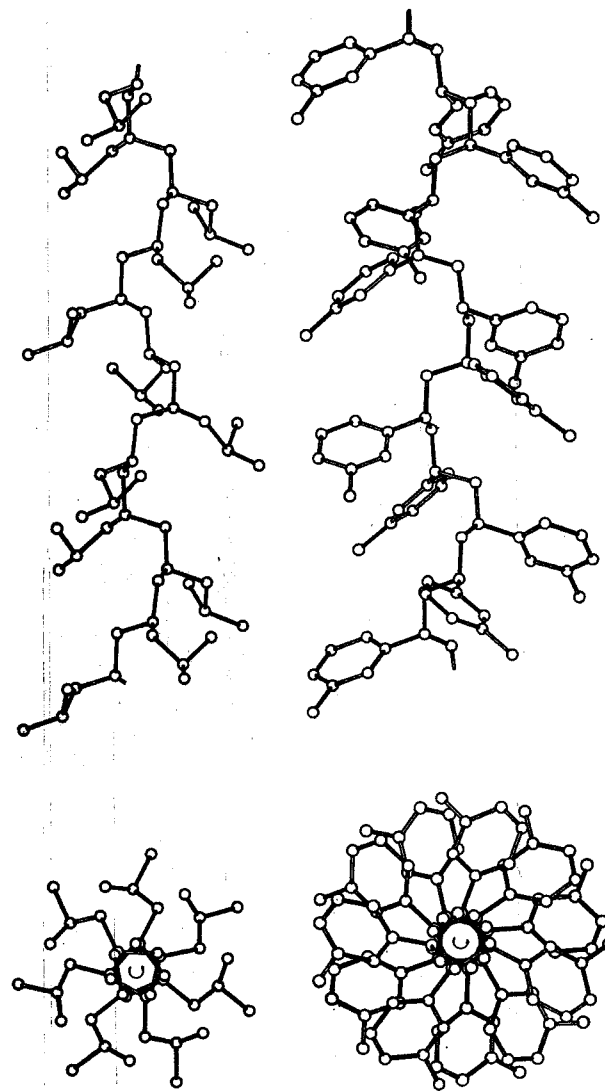

Fig. 3. Polymer chains with 7₂ symmetry (poly-4-methylpentene-1) and with 11₃ symmetry (poly-m-methylstyrene)

iyl naphthalene is crystalline; its isomer, 2-vinyl naphthalene is
rphous[8]).

owever we could demonstrate that some polymers are isotactic even
ey are not crystallizable. This fact had already been foreseen by us
he basis of certain analogies in the course of polymeriza ions, in the
ibution of molecular weights and in the chemical nature of the poly-
.

ow we have demonstrated it in a sure way, with two different meth-
which I briefly summarize below:

One of the methods consists in subjecting amorphous polymers
ained with stereospecific catalysts) to chemical treatments which
ify the steric encumbrance of side groups, without modifying the
i chain structure. For instance among halogenostyrene polymers,
rostyrene polymers are amorphous, even if they are polymerized at
same conditions in which styrene and p-fluorostyrene give crystalline
mers. The complete catalytic hydrogenation of the benzene ring
mpanied by dehalogenation, as accomplished with RANEY-Ni at
°C, turned the amorphous polymers of p-chloro-, of m-chloro-, of
omo-, and of m-fluorostyrene into crystalline polymers[9]).
i Fig. 4 a are shown for comparison the spectra of amorphous poly-p-
rostyrene, of hydrogenated poly-p-chlorostyrene, of isotactic poly-
il cyclohexane; the third showing the same crystalline structure of
second as it also results from the I.R. spectra (see Fig. 4 b).
wing to the fact that we cannot think that the ring hydrogenation
ages the conformation of an atactic chain into an isotactic one, we
t conclude that the main chain of the studied polychlorostyrenes
already isotactic, even if the polymer was not crystalline.
) Another way to explain the lack of crystallinity in some isotactic
mers is the copolymerization of the monomer which gives amorphous
mers with another monomer having slightly different chemical na-
, shape and size which under the same conditions of polymerization
s crystalline isotactic polymers. For instance p-methylstyrene which
itself gives amorphous homopolymers, copolymerized with styrene,
s crystalline polymers having unit cell of the same type of iso-
ic polystyrene and values of the lattice constants in the direction
mal to the chain axis, slightly different from those of isotactic poly-
ene and increasing with the increase of the percentage of p-methyl-
ene.
he identity period along the chain axis, corresponding to 3 monomeric
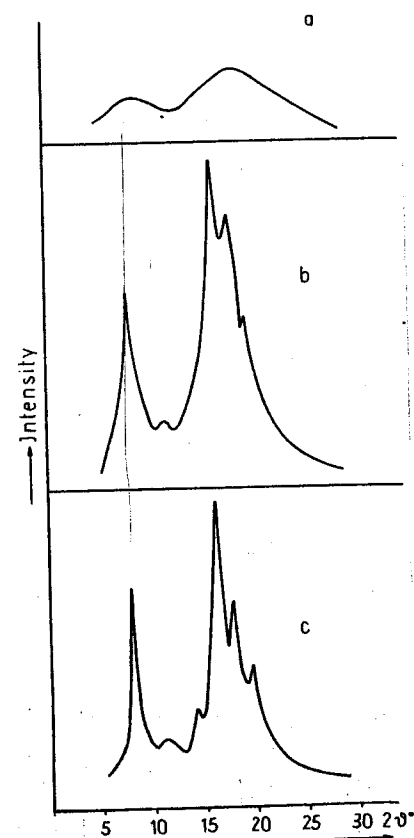s (6.65 Å), keeps unaltered.

Fig. 4a. X-ray powder spectra (Cu Kα) registered with a GEIGER counter of: a) Isotactic amorphous poly-p-chlorostyrene, b) hydrogenated and dehalogenated poly-p-chlorostyrene, c) Isotactic polyvinyl cyclohexane

Extrapolating to the pure p-methylstyrene homopolymer, the X-ray
data observed for styrene copolymers containing from 0 to 50 % of
p-methylstyrene, we calculated the following lattice constants:

$$a = b > 25 \text{ A}, \quad c = 6.65 \text{ A}, \quad d < 1.00 \text{ g/cm}^3$$

while the constants of the isotactic polystyrene are:

$$a = b = 21.9 \text{ A}, \quad c = 6.65 \text{ A}, \quad d = 1.12 \text{ g/cm}^3$$

The density of the amorphous poly-p-methylstyrene is 1.04, a higher
value than the one that may be foreseen[7]) for a crystalline poly-p-
methylstyrene isomorphous with the isotactic crystalline polystyrene.

Styrene p-methylstyrene copolymers containing more than 50 % of
p-methylstyrene generally are amorphous, but if they are hydrogenated
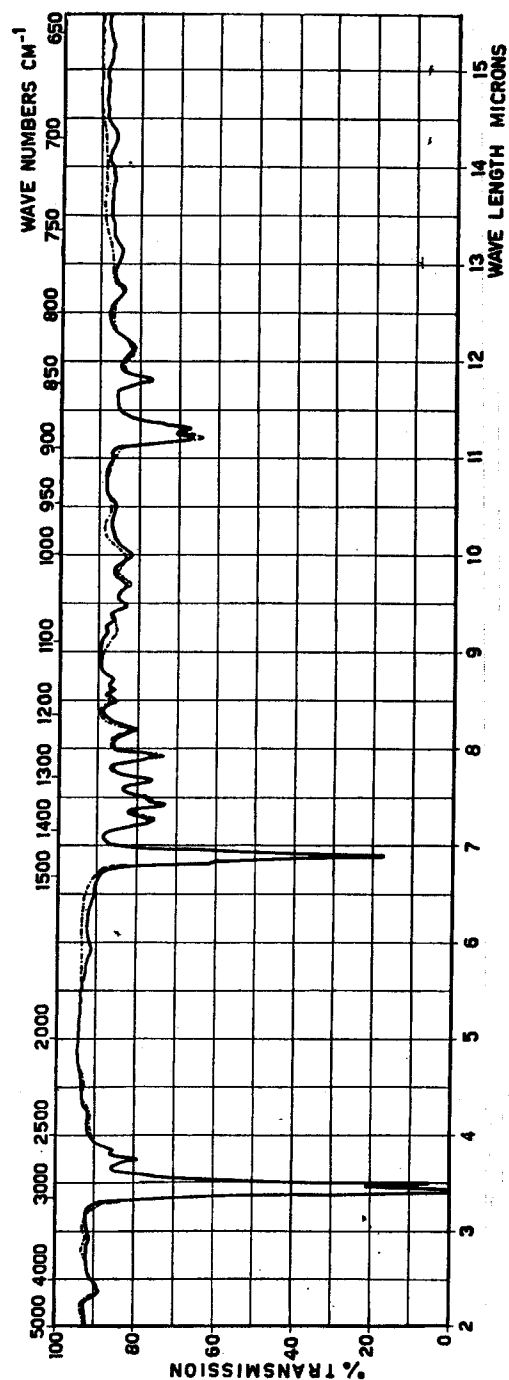they crystallize.

Fig. 4b. I.R. Spectra of isotactic polyvinyl cyclohexane (———) and of hydrogenated and de-halogenated isotactic non crystalline poly-p-chlorostyrene (–·–·–·–)

It is clear that the hydrogenation increases the size of the cyclic group in such a way that the ratio length/width is smaller for the methylcyclohexyl than for the methylphenyl group, thus allowing a better packing of the chains (isotactic helices) in the crystals. It is therefore demonstrated that not all the vinyl polymers with isotactic structure are crystalline.

Independently of the kinetic factors which exert an influence upon crystallization rates, crystallinity is generally achieved only when the best possible packing of the chains (which in isotactic polymers must assume a helicoidal conformation, in which all the monomeric units are equivalent) leads to the formation of crystals whose density is not remarkably lower than that of the amorphous polymer.

Polymorphism in stereoregular polymers

Many cases of polymorphism were observed in the field of polymers with a sterically regular structure. They may depend on many reasons:

1. Phenomena of real polymorphism, due to the existence of different modifications having different crystal structure; each structure is stable in particular conditions: i.e. temperature, pressure, stress. For instance, trans 1,4-polybutadiene, at about 60 °C., turns into a different crystalline modification (Fig. 5) with a shorter identity period along the chain axis
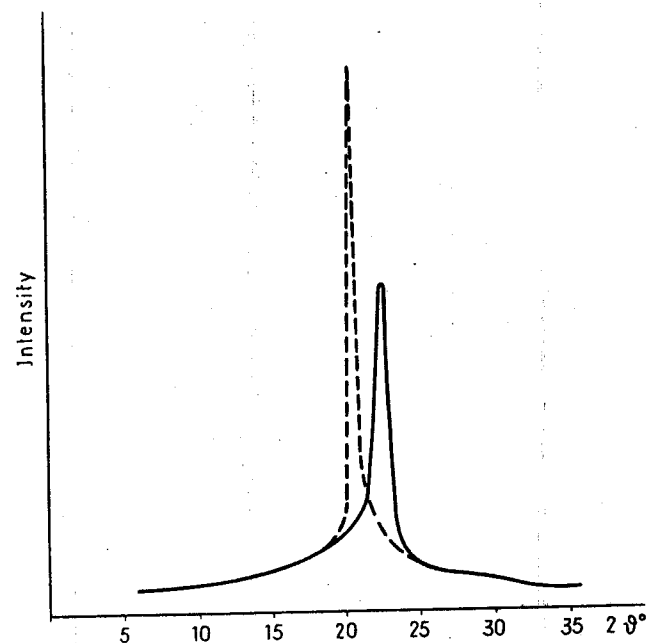

Fig. 5. Comparison between the X-ray powder spectra (Cu Kα) of the two modifications of trans-1,4-polybutadiene (the spectrum of the modification stable at room temperature is full drawn)

103

Å), while the identity period of the modification stable at a low :rature is 4.92 Å. This transformation, in the oriented fibres, is ipanied by a contraction of crystals (which keep oriented) in the ion of the chain axis, parallel with the fibre axis with production chanical work if the fibre is kept under tension
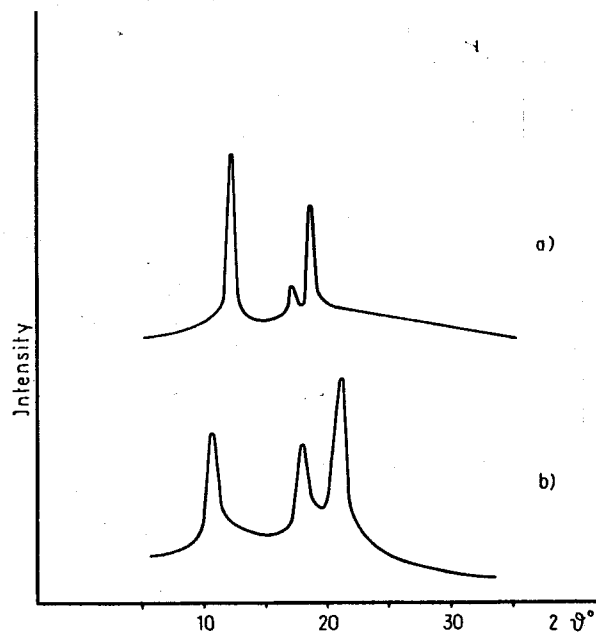

Fig. 6. X-ray powder spectra (Cu Kα) of the two modifications of poly-α-butene:
a) modification 2, b) modification 1

:refore it is possible to consider a thermodynamic cycle, (rever- in theory if viscous flowing were avoided), turning heat into inical work, through the heating of the stretched fibre at a high :rature and the cooling at a lower temperature.
Polymorphism due to the existence of unstable crystalline modi- ins. For instance the poly-α-butene chain can have different con- tions according to the conditions in which the polymer crystal- '); if it is crystallized from solutions, it generally shows a non three- ielix which tends to transform itself into the more stable modi- in of a threefold helix. In Figs. 6 and 7 a comparison is made be- the X-ray and I.R. spectra of these modifications.
Particular polymorphism phenomena may exist when the chains ack in a different way even if they maintain the same helix sym-
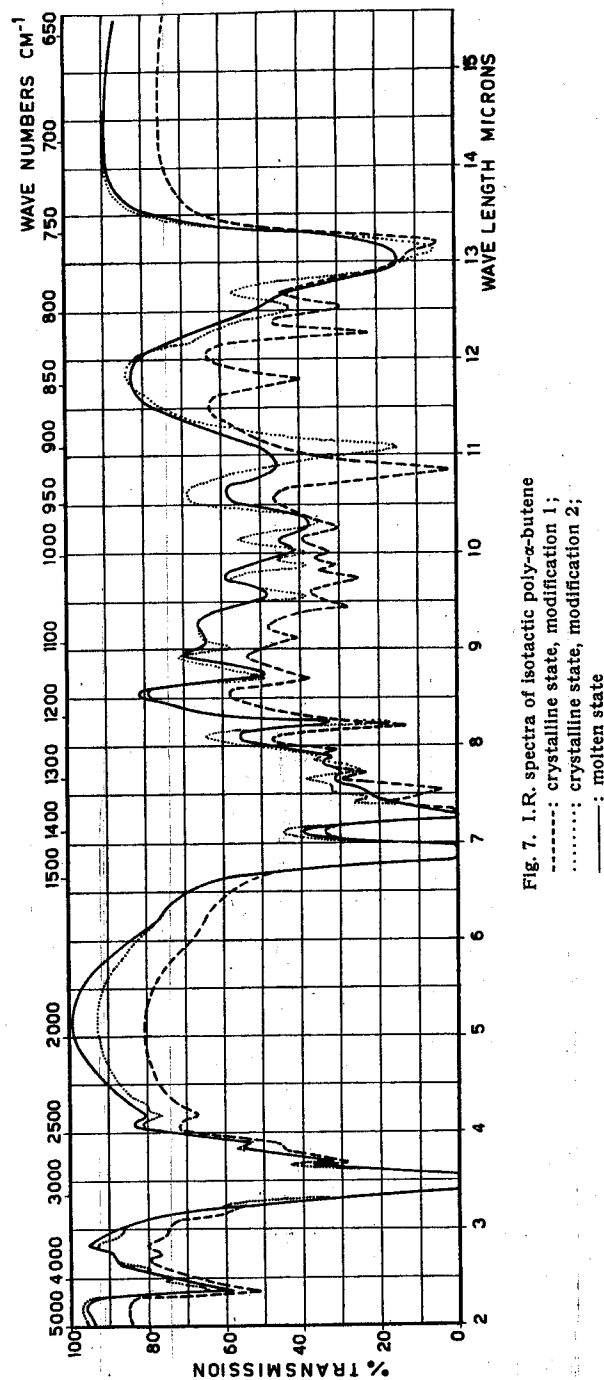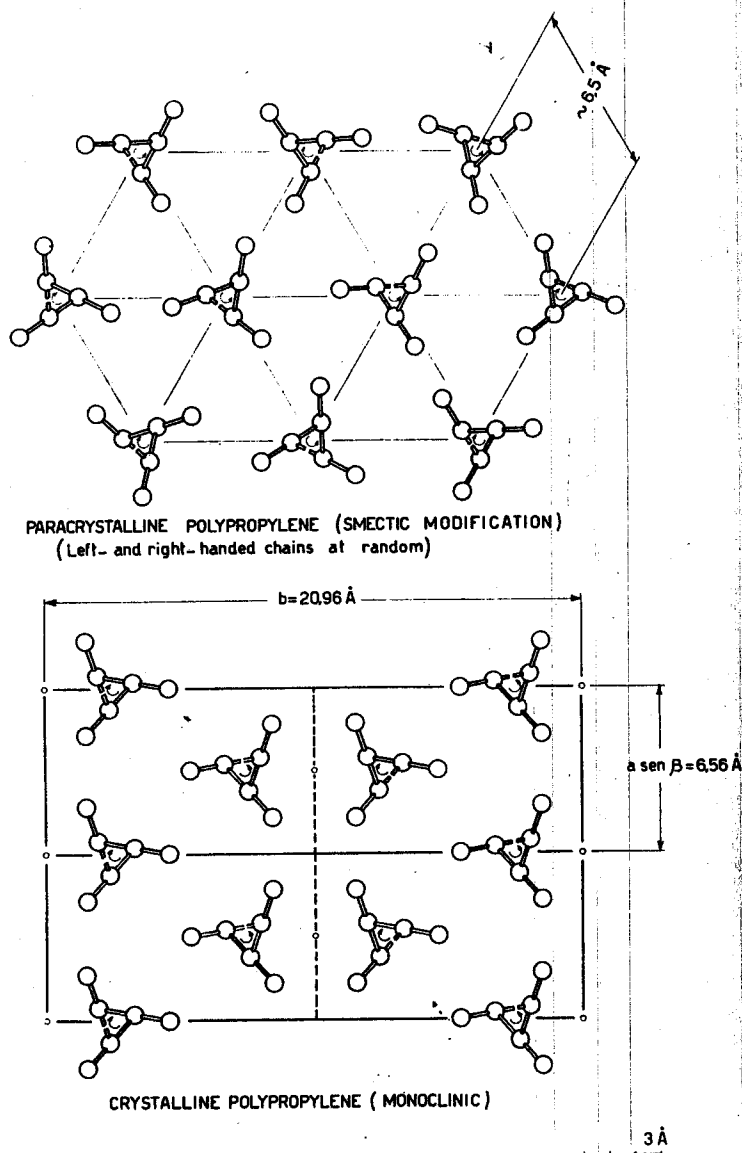

Fig. 7. I.R. spectra of isotactic poly-α-butene
------: crystalline state, modification 1;
········: crystalline state, modification 2;
———: molten state

ry (and therefore the same identity period along the chain axis). In case of the isotactic polypropylene, right-' and left-handed chains γ exist; we must think that usually they are present in equal protions. As it is shown in Fig. 8, in the crystalline modification having monoclinic unit cell (d = 0.94), right- and left-handed helices are

PARACRYSTALLINE POLYPROPYLENE (SMECTIC MODIFICATION)
(Left_ and right_ handed chains at random)

CRYSTALLINE POLYPROPYLENE (MONOCLINIC)

3 Å

. 8. Projection on (0 01) plane of the structure of isotactic polypropylene in its paracrystalline and crystalline modifications

regularly disposed facing one another two by two. By a rapid cooling of the melted polymer we obtained a paracrystalline smectic modification, in which probably right- and left-handed helices are placed at random[11]).
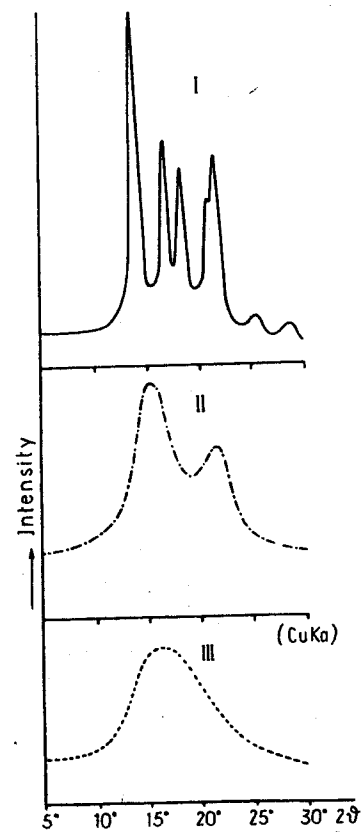
Fig. 9. X-ray powder spectra (Cu Kα) registered with a GEIGER counter of isotactic polypropylene: I) monoclinic, II) smectic (pseudo-hexagonal), III) amorphous

The density value of the latter modification (0.88) is lower than that of the monoclinic modification. Polymeric chains of this smectic form may be oriented by cold stretching (t < 70 °C.) without transformation in the stable modification.

The X-ray spectra (Fig. 9) show that the two modifications have a different structure, whereas the infrared spectra between 7 and 14 microns are practically identical. This is due to the fact that the structure of each chain in both modifications is identical (and the two I.R. spectra
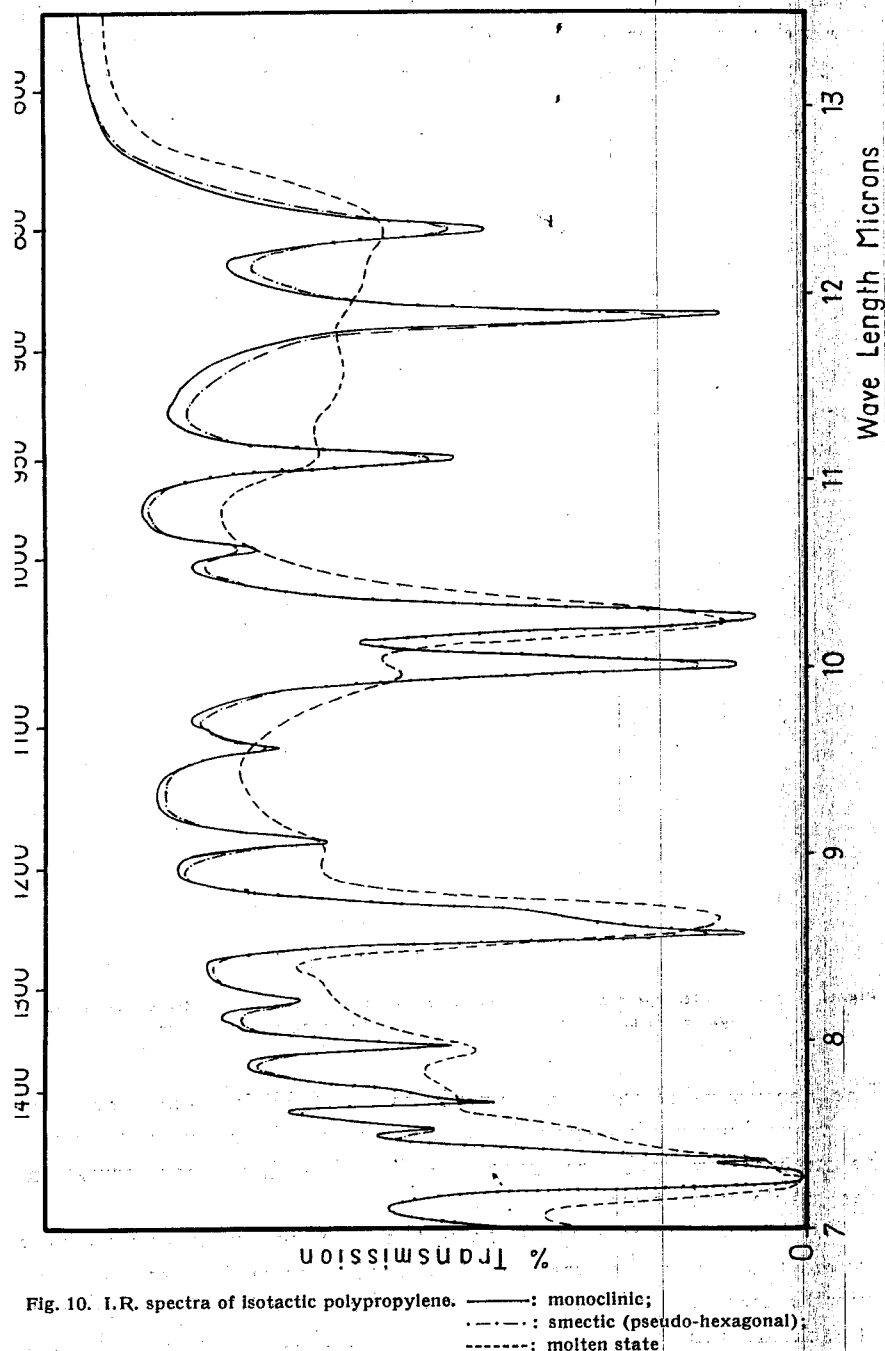
Fig. 10. I.R. spectra of isotactic polypropylene. ————: monoclinic; ·—·—·: smectic (pseudo-hexagonal); -------: molten state

(Fig. 10) are identical because they are practically the spectrum of the isolated threefold helix and nearly independent of the packing of the helices).

4. Polymorphism phenomena of unstable modifications existing only in particular conditions (i.e. in copolymers) will be related in the subsequent chapter on isomorphism and isodimorphism of monomeric units in the polymeric field.

5. Besides the typical cases of polymorphism previously described, we observed for some isotactic polymers the formation of enantiomorphous crystals entirely formed either of right-handed helices or entirely formed of left-handed helices. For instance enantiomorphous chains of the poly-*tert.*-butylacrylate, as shown in Fig. 11, and of poly-5-methylhexene, contrary to what happens for other isotactic polymers (i.e. for polypropylene), give crystals where only isomorphous helices can be present. Only if a right-handed helix can transform itself into a left-handed one through physical processes (i.e. through melting and subsequent cooling) we could speak of real polymorphism.
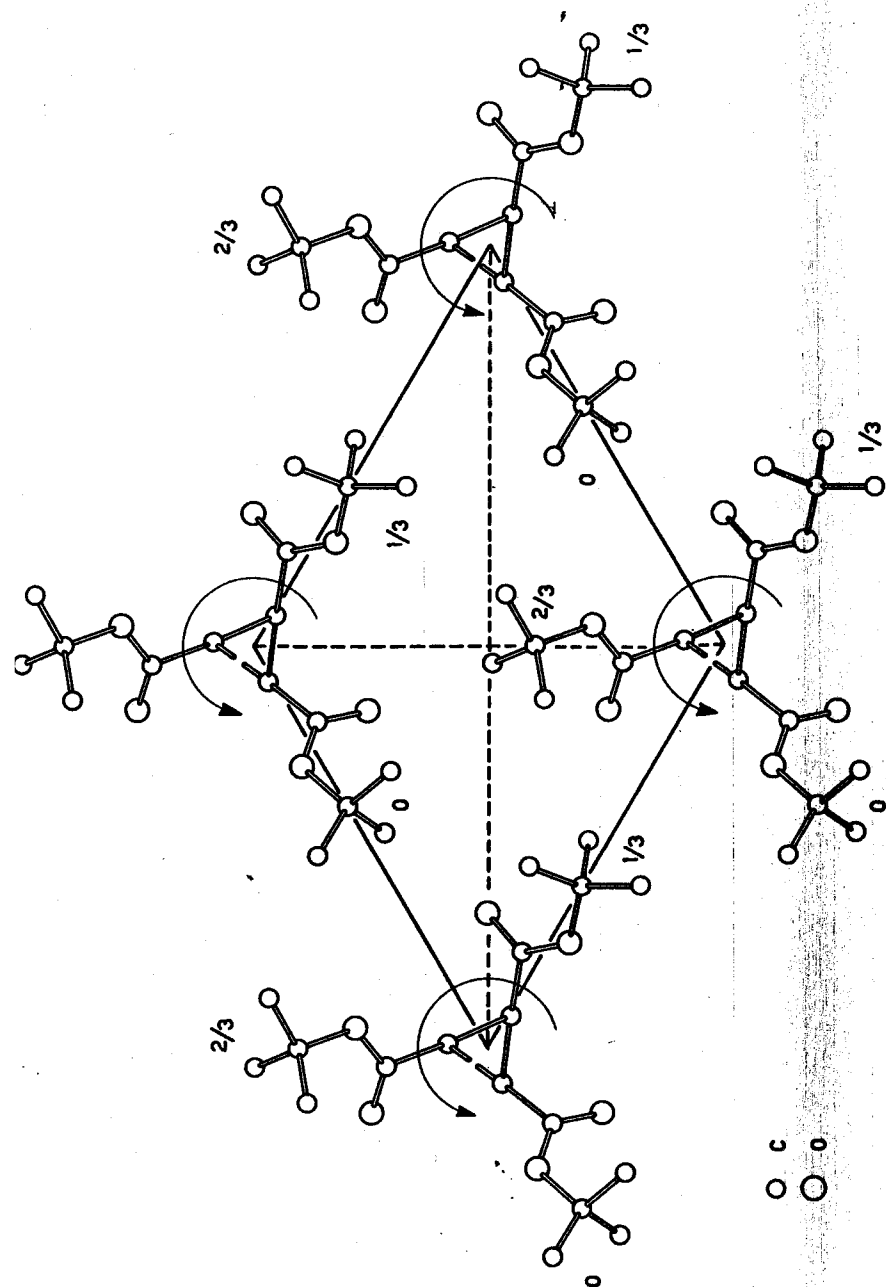
Syndiotactic poly-α-olefins

In 1955 we described[12] the first syndiotactic highly crystalline polymer. It is one of the two polybutadienes with 1,2 enchainment that we obtained by means of stereospecific polymerization of butadiene with metallorganic catalysts formed by reacting certain oxygenated or nitrogenous compounds of transition metals with metalalkyls[13]. According to the type of catalyst and in particular to the ratio between metalalkyls and transition metal compound and to the operating conditions, we obtained atactic, syndiotactic and isotactic polymers with 1,2 enchainment[14]. Also polyvinyl chloride and polyacrylonitrile show a very limited degree of order of the syndiotactic type.

Polymers to which a syndiotactic structure was ascribed, were subsequently obtained from other vinyl oxygenated monomers (methacrylates, etc.)[15]. However from literature it does not appear that syndiotactic polymers of α-olefins have been till now obtained.

Many years ago we tried to produce syndiotactic poly-α-olefins in different ways, but (even if for certain polymers obtained in particular conditions we had long ago observed clues of the existence of a crystalline modification different from the stable isotactic one) only recently we obtained crystalline polymers of α-olefins having a syndiotactic structure, completely free from the presence of a crystalline modification with isotactic structure.

Fig. 11. Mode of packing of isotactic poly-*tert*-butyl acrylate

Among our first attempts, I recall the hydrogenation of diolefinic polymers with 1,2 enchainment, having a syndiotactic structure[16]. Hydrogenation, in the conditions in which the isomerization of the main chain of other stereoordered (isotactic) polymers is not observed (t < 200 °C.), should give a polymer structure corresponding to that of syndiotactic poly-α-butene.

However, even with a practically complete hydrogenation (> 95 %) of 1,2 syndiotactic polybutadiene, it was obtained an amorphous product and therefore not a product having a crystalline structure similar to the non saturated polymer, as it could be foreseen if we admit isomorphism of the vinyl group with the ethyl group in the respective macromolecules.

This is probably due to the encumberment of the $-CH_2-CH_3$ group which is larger than that of the $-CH=CH_2$ vinyl group which, for its size already compels the main chain to assume a conformation which is deformed in comparison with the planar one, and to the fact that such a structure would not satisfy to the principle of the staggered-bonds.

Recently we succeeded in preparing syndiotactic crystalline poly-propylene[17] by direct synthesis from propylene and in obtaining it free from isotactic crystallinity. In the crystalline state it shows a conformation of the main chain very different from the one of the known syndio-tactic polymers (i.e. syndiotactic polybutadiene and polyvinyl chloride) which show planar or nearly planar chain structures. The crystalline structure of syndiotactic polypropylene is interesting[18] because its main chain has a particular helix conformation (Fig. 12). The identity period along the chain axis is 7.3 Å corresponding to 4 monomeric units. This notwithstanding all the monomeric units are structurally equivalent. The main chain, besides the twofold screw axis parallel to the chain axis, shows two twofold symmetry axes normal to the chain axis itself.

For syndiotactic polypropylene, such a chain conformation gives a good packing; this fact explains why the melting point of the syndio-tactic polymer is high, in analogy with what happens for isotactic poly-propylene. In Fig. 12 two enantiomorphous helices of syndiotactic poly-propylene are drawn. The mode of packing of these chains is shown in Fig. 13. With regard to other poly-α-olefins, we can foresee that, in analo-gy with what happens with isotactic polymers, not all the syndiotactic polymers crystallize.

The preparation of syndiotactic crystalline poly-α-olefins, enlarges the field which is already complex of configuration isomers of poly-α-olefins.

or the isotactic polymers, the physical properties and in particular hermic and mechanic ones of syndiotactic polymers depend on their c purity. Different products which remarkably differ one from an- t because of their physical properties and therefore also in their possi- echnical applications, may be obtained and distinguished according eir steric structure and purity.

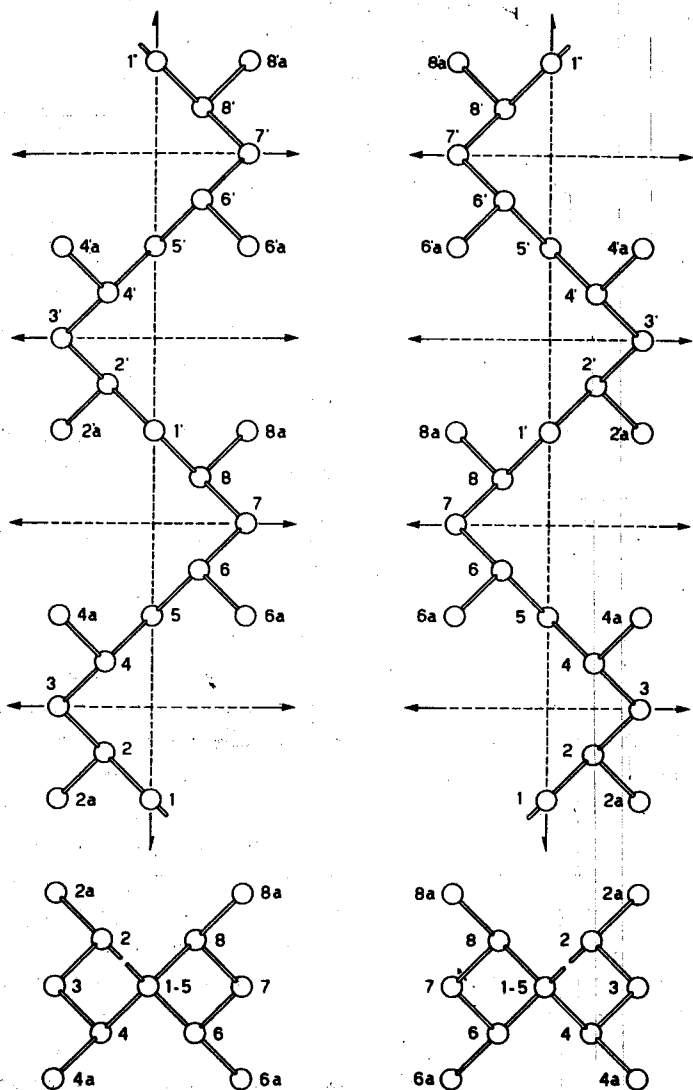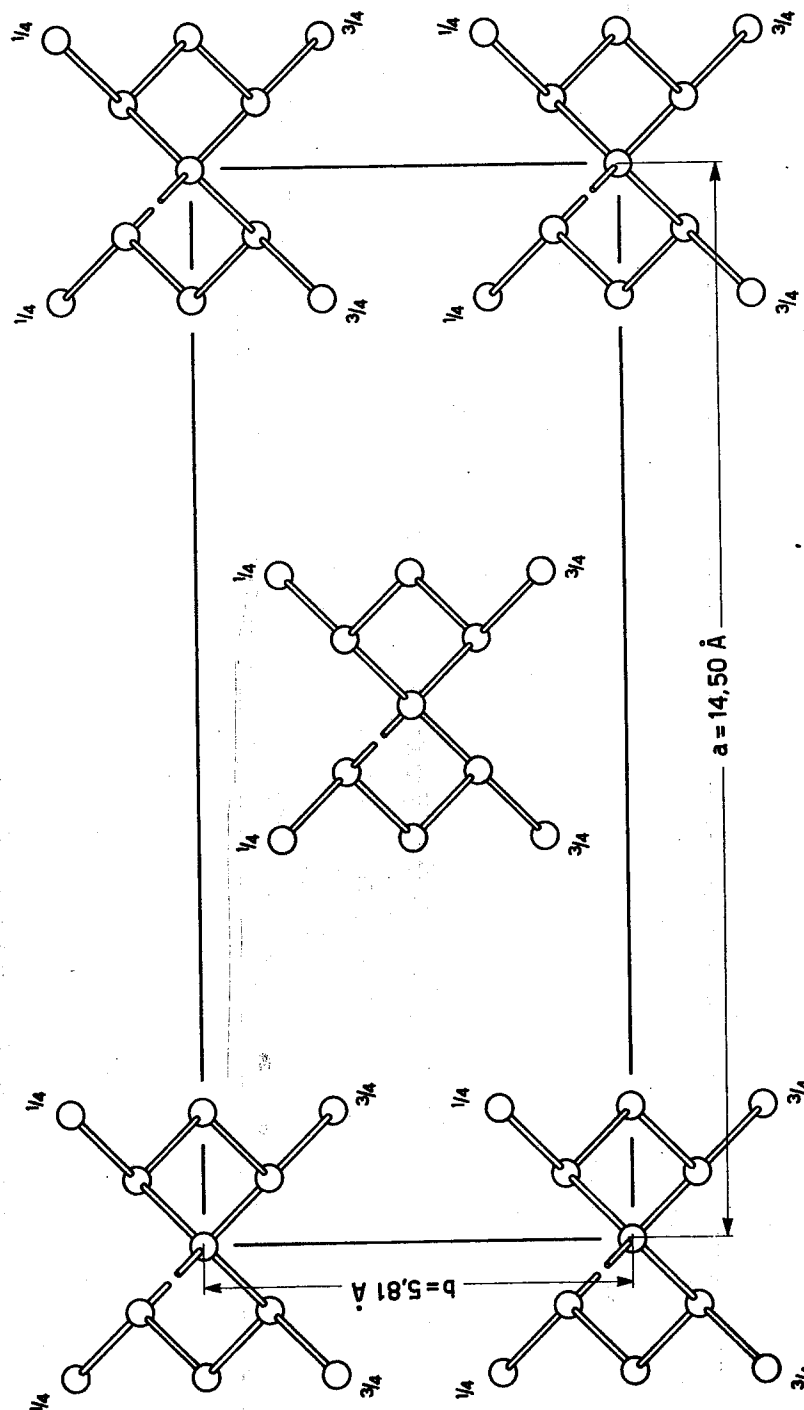ig. 12. Syndiotactic polypropylene. Side and end views of enantiomorphous chains

Fig. 13. Mode of packing of syndiotactic polypropylene

e eventual co-existence in the same chain of isotactic and syndio-
:tic crystallizable parts further complicates the problem of the relation-
p between properties and steric structure of poly-α-olefins.

Isotactic and syndiotactic polymers of vinyl non hydrocarbon monomers

The discovery of isotactic and syndiotactic vinyl polymers roused in
iny research laboratories a big impulse towards the discovery of
reoregular polymers deriving from other types of monomers.
The researches previously accomplished by SCHILDKNECHT on poly-
iyl ethers[19], by PRICE on the polymers of 1−2 epoxides[20], by GARRETT
d MILLER on acrylates[21], and by FOX and GARRETT on methacryl-
:s[15] brought to the description of new crystalline polymers. We pre-
red ourselves a series of crystalline polymers from vinyl monomers
ich contain oxygen, nitrogen, silicon, halogens, etc.; all of them have
isotactic structure and some of them were obtained with a high steric
rity[22].

le 2. Roentgenographic data on some crystalline isotactic non hydrocarbon polymers

Polymer	Chain axis A	Helix type *)
Poly(allylsilane)	6.45	3_1
Poly(allyltrimethylsilane)	6.50	3_1
Poly-5-(trimethylsilyl)pentene-1............	6.55	3_1
Polyvinyl methylether	6.30	3_1
Polyvinyl isobutylether	6.50	3_1
Polyvinyl neopentylether	6.40	3_1
Polyisopropylacrylate.....................	6.50	3_1
Poly-*tert*-butylacrylate	6.45	3_1
Poly-*o*-fluorostyrene	6.63	3_1
Poly-*p*-fluorostyrene	8.30	4_1
Poly-*o*-methyl-*p*-fluorostyrene	8.05	4_1
Polymethylisobutoxyethylene	13.77	7_2

It is to be understood that, besides the right-handed X_n, also the left-handed X_{X-n}
helix exists.

In Table 2 we show the identity periods and the helix types, as obtained
m measurements, performed on some of these polymers[23]. Vinyl-
ier monomers furnish crystalline polymers with catalysts of different
es (preferably with those reacting through a cationic mechanism) if

they are polymerized at a very low temperature. Generally stereospeci-
ficity using soluble ionic catalysts, is limited to low temperatures ranging
from −100° to −35 °C. Just polymerizing branched alkyl acrylates with
heterogeneous catalysts we obtained crystalline polymers having a high
melting temperature and a high crystallinity, even working at room
temperature or slightly above[24].

The anionic coordinated catalysis processes which polymerize α-olefins
in general do not permit the polymerization of monomers with a "lone
electron pair" such as O, N, etc. owing to the fact that these behave as
poisons when they associate with the catalytic complex in a stable way.
A series of coordination catalysts having a cationic or an intermediate
(between anionic or cationic) behaviour act stereospecifically on vinyl-
ethers or on other monomers, which do not polymerize with most of
the known ZIEGLER catalysts.

Di-isotactic polymers

In 1958[25] I already described the first di-isotactic hydrocarbon poly-
mers obtained polymerizing deutero propenes, and more precisely poly-
mers of cis and trans propene-1 d_1, with the typical stereospecific catalysts
of α-olefins (α-TiCl$_3$−AlR$_3$). Working with those catalysts, at the same
conditions in which a good stereospecificity for α-olefins can be observed,
an isomerization of the two geometrical isomers does not occur during
the polymerization (at least not in such a proportion as to mislead the
results).

The two polymers obtained with the cis and trans isomers, are both
crystalline, but their I.R. spectra differ from each other and from the
I.R. spectrum of the crystalline polymer, obtained polymerizing a mix-
ture of cis and trans 1-deutero propene-1. Even though such polymers
observed by X-rays show the same crystalline lattice and therefore cannot
be distinguished by this method, the differences observed in the I.R.
spectra allow us to determine that some stereospecific catalysts (such as
α-TiCl$_3$/Al(C$_2$H$_5$)$_3$), determine during the polymerization the configu-
ration not only of the tertiary carbon atom of the HCCH$_3$ group, but also
of the HCD group.

In fact, the differences existing in the I.R. spectra, in the two types
of crystalline polymers, respectively obtained from the trans and cis
isomers, can be only ascribed to a different, but regular steric order of
deuterium atom in respect to the methyl group. As it results from Fig. 14,

g the structure by X-ray examination identical, and supposing that
:wo polymers are isotactic with respect to thé carbon atom β CHCH₃,
 different and regular conformations (enantiomorphous between
nselves) are possible for the CHD group.

a
THREO-POLY-
(1-DEUTERO-PROPYLENE)
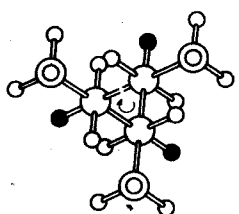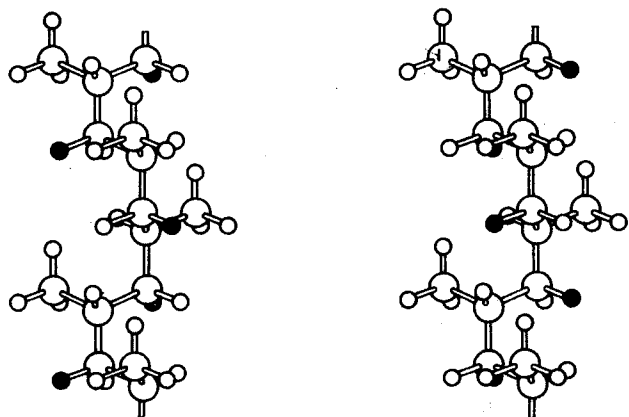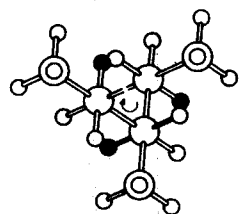
b
ERYTHRO-POLY-
(1-DEUTERO-PROPYLENE)

Fig. 14. Side and end views of the chain of di-isotactic polypropylene 1 d₁:
a) *threo*-poly-1-deutero-propylene
b) *erythro*-poly-1-deutero-propylene

n Fig. 15 the two types of chain are schematically drawn in the same
y previously used to describe the polymers which are simply isotactic,
posing that the main chain is stretched on a plane. In one case all the
iterium atoms D are situated on the same side of the methyl groups,
he other case on the opposite side. In both cases there is an isotactic

structure for the CHD groups. The chain is therefore formed of successions
of CHD groups, which are isotactic among themselves, and of CHCH₃
groups, which are also isotactic among themselves, and therefore we call
"di-isotactic" the polymers showing a double isotacticity in the main
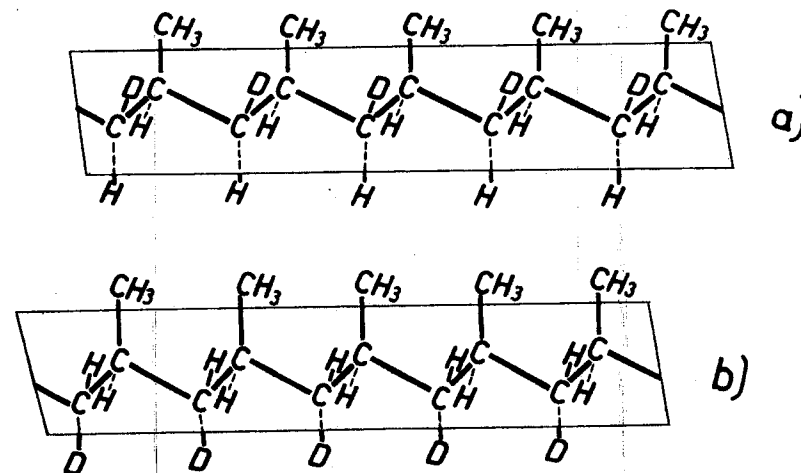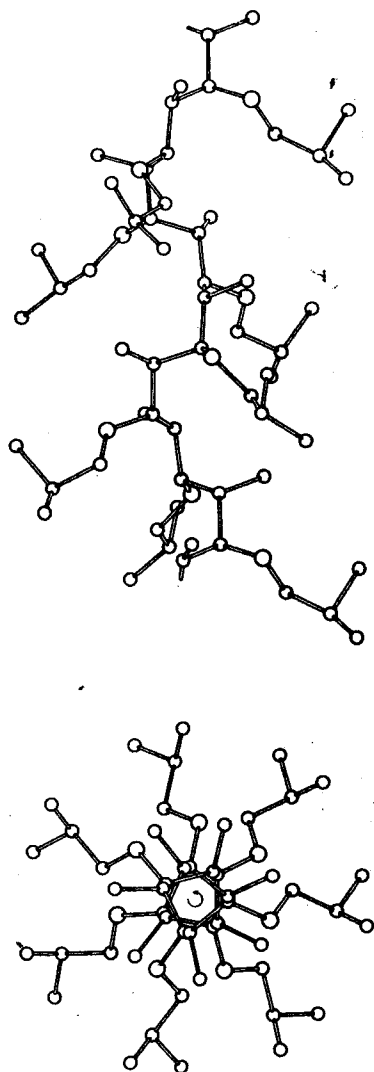chain.

Fig. 15. Schematic drawing of di-isotactic polypropylene 1 d₁:
a) *threo*-poly-1-deutero-propylene
b) *erythro*-poly-1-deutero-propylene

For the two different types of structure, we used the prefixes "threo"
and "erythro" to distinguish polymers in which a substituent respectively
is, in the drawing shown in Fig. 15, on the same side (a) or on the opposite
side (b) of the other substituent.

Other di-isotactic polymers have been obtained in our Institute poly-
merizing monomers of the CHR=CHR' type, where R and R' are different
chemical groups[26]). For these polymers we could demonstrate that from
the trans isomer it is possible to obtain the threo-di-isotactic polymer.
In Fig. 16 it is shown the chain conformation with 7_2 symmetry of threo-
di-isotactic 1-methyl-2-isobutoxyethylene, obtained by direct synthesis
with stereospecific catalysts which act on the internal double bond.
This compound is not only the first di-isotactic polymer possessing a
remarkable chemical difference among the substituents in both tertiary
carbon atoms, but it is also the first example of crystalline isotactic
polymer of a monomer containing an internal double bond. In fact all
the isotactic polymers previously known, whose main chain is exclusively
formed of carbon atoms, were polymers of vinyl monomers.

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The discovery of new important series of crystalline polymers obtainable by stereospecific polymerization, allowed us to observe different types of isomorphism in the macromolecular field. These isomorphism phenomena cause continuous variations, in relation to their composition, of some parameters of the crystalline lattice, in analogy with what happens in solid solutions of substances of low molecular weight (Fig. 17).

16. Side and end views of the chain of crystalline *threo*-di-isotactic poly-methylisobutoxyethylene (helix type 7₃)
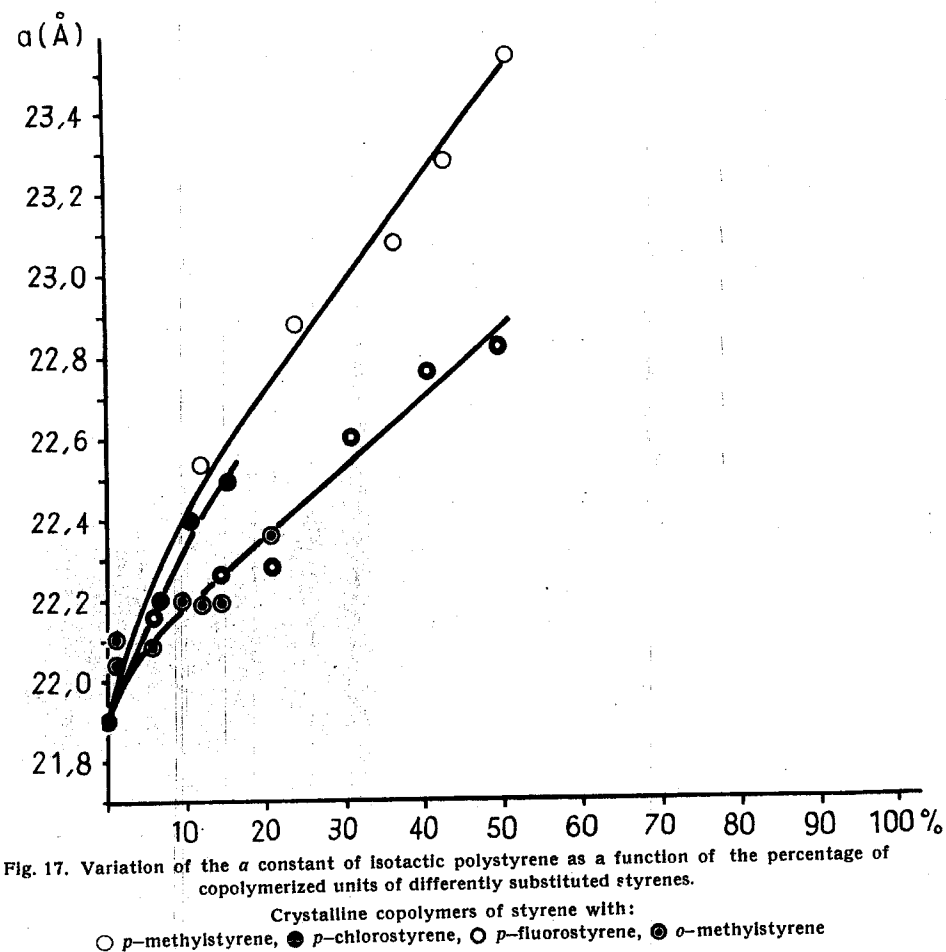

Fig. 17. Variation of the a constant of isotactic polystyrene as a function of the percentage of copolymerized units of differently substituted styrenes.
Crystalline copolymers of styrene with:
○ p–methylstyrene, ● p–chlorostyrene, ◐ p–fluorostyrene, ◉ o–methylstyrene

Isomorphism phenomena in the field of linear macromolecules

Whereas the isomorphism phenomena in the field of the mineral and ~~org~~anic (low molecular weight) substances have been deeply studied, ~~the~~ same phenomena in the macromolecular field were not, because the ~~nu~~mber of the known crystalline polymers available for a systematic ~~stu~~dy was still limited.

It is possible to foresee different types of isomorphous substitutions in the lattices of crystalline linear macromolecules. Here we point out some typical cases:

1. Isomorphism of macromolecules

This isomorphism has been observed when macromolecular chains with little different chemical nature or structure, which have almost the same

entity period along the chain, and do not differ — or differ very little —
the transversal dimensions, pack themselves in the same crystalline
:tice forming solid solutions.

For instance we observed isomorphism in the following cases:

a) An isomorphous substitution among the helix chains having the
me spiral direction but a different orientation (up or down) of the side
ɔups akes place, for instance, in some α-olefin polymers (but not in all
them). When this substitution can take place, it does not modify the
le dimensions of the lattice[3]).

b) On the contrary the random substitution of right-handed helix
ains with left-handed helix chains causes, when it takes place, para-
γstalline unstable structures (smectic form of polypropylene) which
ɔ looser even if they show the same identity period of the stable form[11]).

c) A solid solution of polymers formed by isotope atoms naturally does
ɪ modify the lattice constants. The I.R. spectra of solid solutions of
lypropylene and of poly-deuteropropylene present a continuous linear
riation of the intensity of certain bands in relation to the composition
the polymer.

On the contrary a propylene deutero-propylene copolymer has the
ne X-ray spectrum and the same lattice constants, but shows re-
ɪrkable variations of some crystallinity bands according to the com-
sition at the I.R.; these bands disappear, when the percentage of one
ɪnomer ranges from 33 to 67 %[25]).

1) Solid solutions of macromolecules can be foreseen among polymers
different monomers, characterized by the same type of lattice struc-
·e, by the same identity period of the main chain and only by small
ferences in the form and size of the side groups. Solid solutions of this
ɔe should be easily prepared when the melting temperature or the
ubility of the two polymers are not very different, so that their
ɪtemporaneous separation in the solid form from their liquid
xtures is possible.

·) Chain isomorphism, allowing true solid solutions, have been ob-
ved by us co-crystallizing chains of homopolymers and crystalline
ɔolymers (i.e. styrene — p-methylstyrene) which show the same identi-
period[27]). The solid solutions exhibit lattice constants which are inter-
diate between those of the employed copolymer and of polystyrene
ɔending on the relative proportions (Fig. 18).

Isomorphism phenomena among monomeric units[27])

ɪ) This very peculiar and new case of isomorphism sometimes hap-
ɪs, when copolymerizing monomers which have chemical nature, shape

and dimensions slightly different one from another and at the same time
are able to give homopolymers having an analogous crystalline structure,
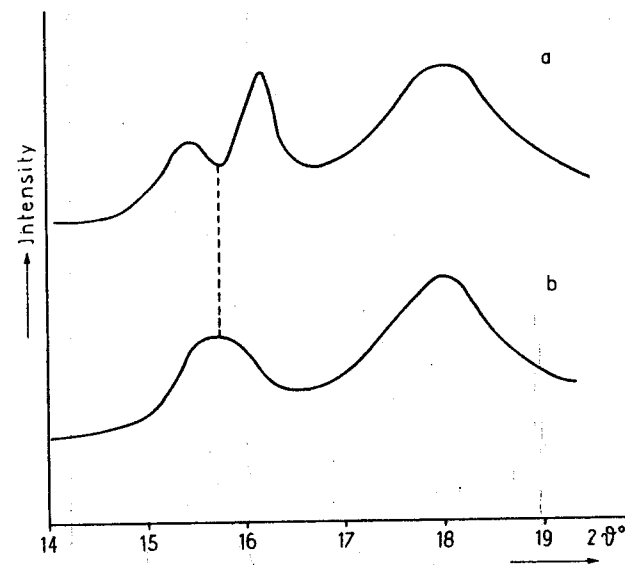the same identity period and slightly different lattice constants.

Fig. 18. X-ray powder spectra (Cu Kα) registered with a GEIGER counter of: a) mechanic mix-
ture, 50 % isotactic polystyrene, 50 % styrene-p-methylstyrene copolymer (molar fraction 30 % of
p-methylstyrene), b) the same mixture after fusion and annealing at 180° C.

In those cases we observed that also the copolymers are crystalline and
have physical properties varying in a continuous way as a function of the
composition of the copolymer; for instance the lattice constants are
intermediate between those of the pure homopolymers.

Whereas, generally, the introduction by copolymerization of non iso-
morphous monomeric units lowers the melting point, according to the
well-known FLORY formula, till the obtainment of amorphous polymers,
it has been now observed that the random introduction of isomorphous
units causes a continuous variation of the melting point which,
generally, assumes intermediate values among those of the pure
homopolymers (Fig. 19). The regular variations of many physical
properties follow the analogies existing with the isomorphism
phenomena previously known for molecules of isomorphous ions, even if
in the copolymers here described the monomeric units are linked by
chemical bonds and they cannot be separated by physical means, as it
happens in the normal solid solution among isomorphous products. The
phenomenon which we shall call *"isomorphism among monomeric units"*

s been observed by us in different systems, at least in some composition nges. With regard to vinyl polymers, we have to think that isomorphous monomeric units which are present in the same chain, must also show the me steric configuration. With regard to o-fluorostyrene and styrene polymers which exhibit the same crystalline structure and practically e same lattice constants, there is isomorphism for all the compositions.
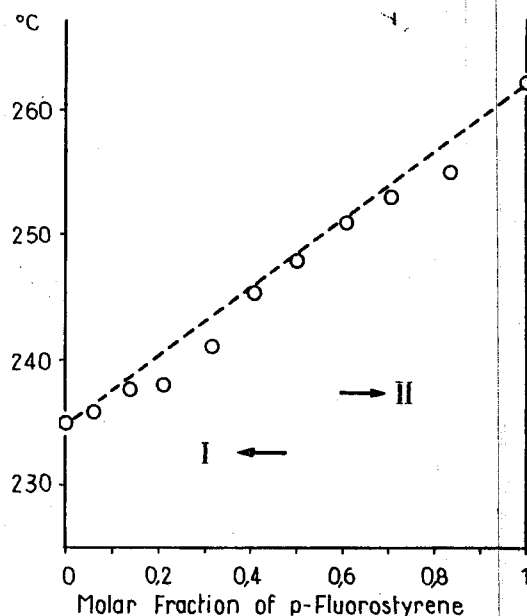

Fig. 19. Melting temperature of crystalline styrene and p-fluorostyrene copolymers
I Crystallites with threefold helix
II Crystallites with fourfold helix

he X-ray spectra always show a high crystallinity while the I.R. ones ow a quick lowering of crystallinity as the content of the component ntained in a lower quantity increases. The disappearence of some I.R. ystallinity bands takes place for contents ranging between 30 und 70 % one of the two components. The comparison between the crystallinity riations observed by the I.R. and the X-ray examinations, allowed us improve our knowledge on the relationship existing between the struc- re and the crystallinity of systems formed by polymers and by differ- t copolymers.

Whereas, in the I.R. spectra, the crystallinity bands are due to inter- tion of the atoms belonging to the same chain, which in the crystals

assumes a regular conformation, the X-ray spectra show the regularity of packing of the chains, which may subsist even if small irregularities due to the presence of different isomorphous monomeric units in the single chains exist.

b) *Isodimorphism.* Crystalline modifications have been observed even in some cases in which homopolymers show different crystalline structures. In the case of isotactic styrene and p-fluorostyrene polymers, for instance, the stable modifications of the homopolymers exhibit different sym- metries. Nevertheless these copolymers are crystalline: the richer in styrene exhibit the structure of isotactic polystyrene stable form (threefold helix), those richer of p-fluorostyrene show the structure of the p-fluoro- styrene stable form (fourfold helix). Therefore there is a particular type of isomorphism which, in analogy with what is observed for the solid solutions of crystalline products of low molecular weight, can be called "isodimorphism". We can admit the possibility of existence of the same crystalline modification in the copolymer for both monomeric units even if sometimes it is unstable (or even more it does not exist) for one of the two pure homopolymers.

It is interesting to note that the introduction of a monomeric unit of bigger size (i.e. p-fluorostyrene, p-methylstyrene, etc. in the polystyrene chain) always causes a remarkable deformation of the lattice constants; this fact does not always happen in the opposite case, that is when a smaller monomeric unit is introduced (i.e. introduction of styrene in the poly-p-fluorostyrene chain).

The formation of mixed crystals, for the styrene-o-fluorostyrene sys- tem, is possible because of the same identity period and the small differ- ences in the dimensions of fluorine and hydrogen atoms.

The lattice constant in the direction of the chain axis results, there- fore, unvaried, while a slight variation of the lattice constants in the directions normal to the chain can be observed.

c) *Isomorphism in systems with crystallinity in a limited composition range.* In some cases monomers giving only amorphous homopolymers, if copolymerized with monomers giving crystalline homopolymers, can form crystalline copolymers. This can be observed when the monomeric units of the component, whose homopolymer is amorphous, are present in the copolymer in small quantity, even if this quantity is sufficient to modify remarkably the copolymer lattice constants in comparison with those of the crystalline homopolymer. This is what happens with the isotactic copolymers between styrene and p-chloro- or p-methylstyrene. These

talline copolymers and the homopolymers which are, on the con-
y, amorphous, are obtained by means of the same polymerization
hanism at rates which are only slightly different from those of styrene
;. 20).
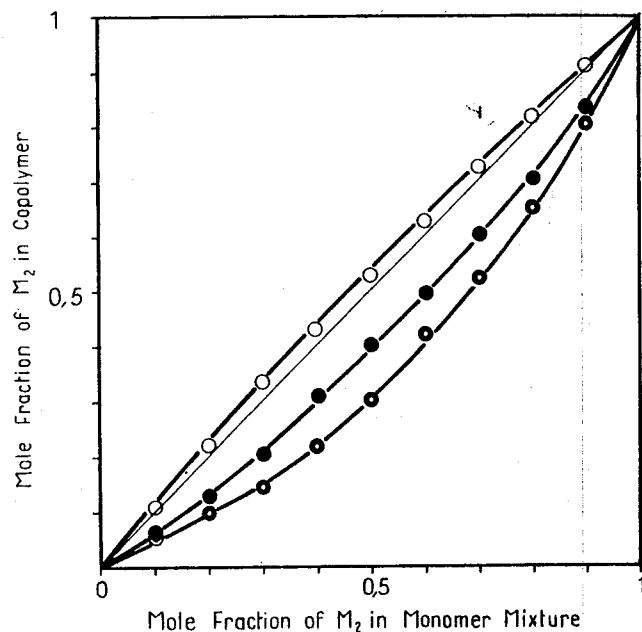
20. Composition curves of stereospecific copolymerization of styrene with differently substituted styrenes (titaniumchloride-aluminium triethyl catalytic systems, t = 40° C)'

M₂: ○ = p–methylstyrene   ● = p–fluorostyrene   ◑ p–chlorostyrene

s we already suggested, it is extremely interesting in the study of co-
merization, to compare the crystallinity data obtained by the I.R.
X-ray spectra.

7ith regard to the I.R. spectra (Fig. 21) many crystallinity bands
e from regular interactions among atoms belonging to the same chain
ch, generally, has a regular conformation only in crystals. The I.R.
tallinity, however, does not depend on the packing regularity in the
imensional lattice, owing to the fact that interactions among atoms
nging to different chains exercise a scanty influence on the crystal-
y bands, at least in the wave length field we have considered. On the
:rary, in the case of X-ray spectra (Fig. 22) definite reflections are
iible only if a regular chain packing in a tridimensional crystalline
ice occurs. Crystals formed by a solid solution of chains of different
iopolymers must also have the I.R. crystallinity bands of each chain.

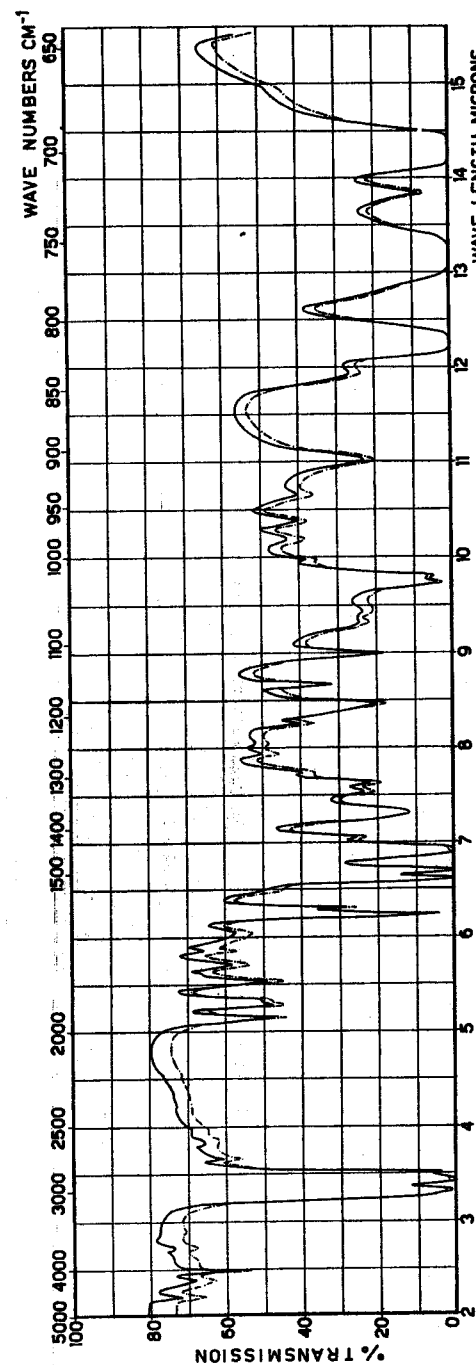Fig. 21. I.R. spectra of a styrene-p-methylstyrene copolymer with a content of 35 % in moles of p-methylstyrene

———: before annealing, –·—·—·: after annealing

some chain transfer processes, with the concentration of metallorganic
npounds in solution.

rthermore we observed by the I.R. spectra that also the polypropylene
in sections which cannot be crystallized may be of two different types:
) Some of them are characterized by a greater number of couples of
acent monomeric units having the same steric configuration. 2) Some
ers, present in the polymers having syndiotactic structure, are charac-
ized by a greater number of couples having opposite steric configu-
ions[31]).

Polymerizing diolefins or monomers containing a lone electron pair,
reospecific polymerizations are possible even without the presence of
olid crystalline component in the catalytic system, and sometimes
n with completely soluble catalysts, especially when the reaction is
ried out at low temperature. This happens, for instance, in the poly-
rization of butadiene to 1,2 isotactic and syndiotactic polymers, in
polymerization of vinyl ethers and of acrylates to isotactic poly-
rs[22]). In these cases the reasons for a lower stereospecificity may be
lifferent nature. One of the most important, but not the only one, may
isists in the chemical impurity of the catalytic complex.

For instance, there are catalytic systems prepared with the same
gents which, according to the ratios of the components and the
rating conditions, furnish isotactic or syndiotactic polybutadienes or
cromolecules of the two types and at the same time atactic macro-
lecules[13, 14]).

As regards polybutadiene with a high value of cis 1,4 content, the way
h which the steric impurities are distributed is more important than
steric purity itself.

Some catalytic systems [obtained, for instance, from TiJ_4 and
$C_2H_5)_3$[32])], give random copolymers of monomeric units with differ-
configurations; because of that, in this case, also polymers having
igh value of cis 1,4 units (about 93 %) show a low melting tempera-
e (in the range of −8 to −10 °C.).

As regards the cis 1,4 unit content in polybutadienes, the here reported
a were determined according to a method recently developed in our
titute[33]).

There are other catalytic systems prepared from other Ti halides[34])
ich give mixtures of macromolecules: among them, some are almost
npletely trans 1,4 whereas others are almost completely cis 1,4.
en if the raw polymers have a low percentage of cis 1,4
's, it is possible, by solvents fractionation to separate macromolecules

which are very rich in cis 1,4 units (92—95 %); these macromolecules
melt at about 0 °C and crystallize rapidly under stretching even at
temperatures above room temperature and even in a relatively high-
vulcanized state[35]).

In this case we can think that the steric impurities are not statistically
distributed along the chains and this allows the existence in the macro-
molecules of sections containing cis 1,4 units sufficiently long to have
a melting point very close to the one of the sterically pure polymer[36]).

From these results we could notice the importance of the distribution
of steric impurities and we undertook a systematic study of the polymeri-
zation of butadiene in order to develop highly selective and stereo-
specific catalysts. The result was that, at the DONEGANI Institute in
Novara[37]) and at the Polytechnic of Milan, raw polymers were synthesized
which are very rich in cis 1,4 units. The melting point of raw polybuta-
dienes with a percentage of cis 1,4 units higher than 99 % is about + 1 °C,
and the melting enthalpy about 2000 cal./mole[36]).

Both for trans 1,4 and cis 1,4 polybutadienes we are able today to
obtain with the stereospecific catalysis raw polymers which are sterically
purer (> 99 %) than natural rubber (steric purity about 97 %) and than
synthetic polyisoprenes, as far as it is reported in the literature.

The increase in steric purity is related not only to a change in certain
properties but beyond certain limits we observe the appearence of new
and very interesting properties which are typical of sterically very pure
polymers.

Table 3. Melting temperatures of linear cis 1,4-polybutadienes having different steric purity
($\Delta H_u = 2,000$ cal/monomeric unit)

% cis 1,4 monomeric units	calculated melting point (°C)
100	+1
98.5	0
95	−3
90	−7
85	−11
80	−15
75	−19

Note: The calculated data take into account only the irregularities due to the presence
along the polymer chain of trans-1,4-butadiene units or of butadiene units with 1,2 en-
chainment.

n the case of cis 1,4 polybutadienes only the presence of long sections chains which are sterically very pure permits the obtainment of vulcand products which, in the absence of reinforcing agents, exhibit an stic behaviour similar to natural rubber[25]). This behaviour is characterd by a remarkable increase of the elastic modulus, even in a wide range temperatures above room temperature, as the deformation increases. is variation is due to the crystallization of the chains which line up allel under stress. In certain temperature ranges the dynamic proper-s of cis 1,4 polybutadienes are higher than those of cis 1,4 polyisoprenes. When considering all the results which have been obtained during five rs of research in the field of the stereospecific polymerization one be really satisfied that the science of macromolecular chemistry is gressing with a rhythm not inferior to the one which is observed in er branches of science. In the field of synthetic rubbers and textiles, ne new products cannot be any longer considered only substituents of tural products (whose use is justified only from economical reasons); fact these new products represent a qualitative progress because they ve properties which are suitable for new and very valuable appli-ions.

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