

Isomorphism Phenomena in Macromolecules

G. NATTA, P. CORRADINI, D. SIANESI, and D. MORERO, *Istituto di Chimica Industriale del Politecnico, Milan, Italy*

INTRODUCTION

A preliminary discussion of different types of isomorphism that may possibly occur in macromolecular substances was presented by one of us at the International Congress of Macromolecular Chemistry held in Wiesbaden in October, 1959.¹ The present paper contains further details of our work in this field.

It is well known that isomorphism is often observed in inorganic compounds, and has been particularly studied in the cocrystallization of different ionic compounds, when the ions differentiating them are of almost equal size and, usually, equal valency. Isomorphism phenomena of this type are also observed in some inorganic macromolecular compounds, for instance, in some natural silicates, which may be considered as constituted of linear or polydimensional macromolecules.

In the field of organic substances, isomorphic phenomena have often been observed in low molecular weight compounds the molecules of which are analogous in size and chemical nature, such as benzene and thiophene. But these phenomena are less known in synthetic macromolecular organic substances. Before the stereospecific polymerization processes were discovered, the number of crystalline polymers that could be used for systematic research on isomorphism was practically limited to condensation polymers.

Our recent research carried out in the field of stereospecific polymerization and copolymerization of vinylaromatic monomers has allowed us to obtain a great number of crystalline addition polymers and copolymers with an isotactic structure, and to observe interesting isomorphic phenomena in some of them: that is, the possibility of modifying the crystalline lattice of a polymer, owing to the presence in the chain of monomeric units of different types, without destroying crystallinity itself and of causing only continuous and regular variations of some parameters of the crystalline lattice, accompanied by continuous and regular variations of other physical properties.

THE PHENOMENA OF ISOMORPHISM IN MACROMOLECULAR SUBSTANCES

It is possible to foresee two general types of isomorphous substitution in the crystalline lattice of a linear macromolecule: (1) isomorphism of chains, (2) isomorphism of monomeric units.

Chain isomorphism occurs when solid solutions of macromolecules are formed by cocrystallizing of different polymers, at least one being crystallizable by itself. This, in the field of macromolecules, is a phenomenon corresponding to that taking place in the formation of solid solutions among isomorphous substances of low molecular weight.

Isomorphism of monomeric units corresponds, on the other hand, to an entirely different conception. It defines the possibility of introducing monomeric units of a different structure statistically along the chains of a crystallizable polymer without hindering the crystallization of the resulting copolymer, but causing just variations of some lattice constants. This type of isomorphism differs from previously known types because it takes place among parts of molecules (monomeric units) linked by stable covalent bonds. Isomorphous monomeric units in the same chain cannot be separated one from another by physical means (for instance, by solution or by melting).

Before examining various examples of isomorphism phenomena in detail, it is useful to point out the value and meanings of the two main methods we used to determine the structural properties of the polymers studied: (a) From x-ray diffraction spectra, it may be established whether macromolecules are orderly packed in a tridimensional lattice. An ordered packing of the chains is maintained in all cases of isomorphism in polymers. Accordingly, the presence of sharp lines in the x-ray spectrum of a random copolymer constitutes a proof of isomorphous substitution of monomeric units. (b) On the contrary the infrared bands, which are generally associated with crystallinity, do not depend on the regularity of packing of several chains in a lattice. They are due mainly to the interaction taking place between atoms repeating themselves in an orderly fashion along an axis, as happens in most crystalline polymers.² Thus, owing to their origin, the IR bands generally associated with crystallinity tend to disappear, in particular when different monomeric units are randomly distributed in the chain, even if the x-ray spectrum is still indicative of regular tridimensional repetition.

(1) Isomorphism of Chains

This type of isomorphism takes place when macromolecules of different kinds are able to pack together in the same crystalline lattice, thus forming real solid solutions. The phenomenon has been observed only when the macromolecular chains have identity periods which are equal or almost equal and when they do not differ, or differ very little, in the dimensions normal to the chain axis.

A particular case consists in the isomorphous substitution between helicoidal all right-handed chains (or all left-handed) differing in the orientation (up or down) of the side groups. This substitution takes place in some isotactic crystalline poly- α -olefins, without modification of the side dimensions of the crystalline lattice.³ In the same way, the formation of solid solutions among polymers containing isotope atoms (such as poly-

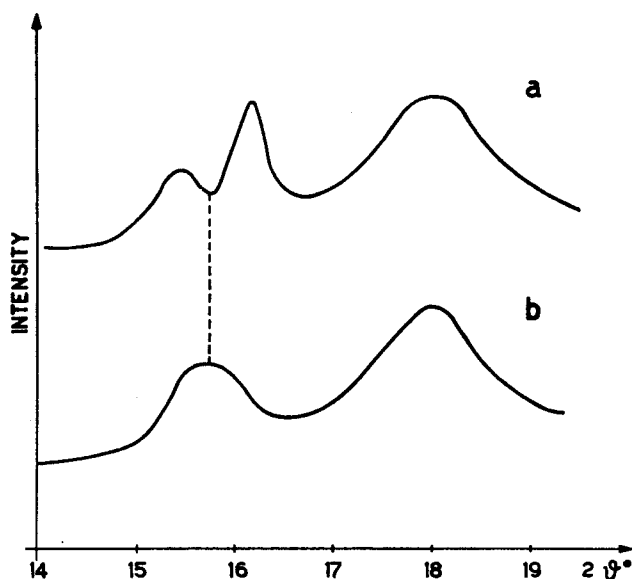


Fig. 1. X-ray powder spectra ($\text{CuK}\alpha$) registered with a Geiger counter of: (a) mechanical mixture, 50% isotactic polystyrene, 50% styrene-*p*-methylstyrene copolymer (molar fraction 30% of *p*-methylstyrene); (b) the same mixture after melting and annealing at 180°C.

propylene and polydeuteropropylene) does not appreciably modify the lattice constants.⁴ The statistical substitution in the same lattice site of right-handed helicoidal chains with the corresponding left-handed ones, causes, on the contrary, when it takes place, the formation of an unstable paracrystalline structure (for example, the smectic form of isotactic polypropylene).

A true chain isomorphism was observed by us when cocrystallizing chains of isotactic polystyrene and of crystalline styrene-*p*-methylstyrene copolymers. The solid solutions have lattice constants that are intermediate between those of the copolymer and those of polystyrene and which depend on the relative proportions of the two components. The formation of solid solutions is possible because the two different polymeric components are characterized by the same crystalline structure and by the same identity period along the chain axis, and show only small differences in the equatorial lattice dimensions.

The formation of solid solutions appears from the x-ray diffraction spectrum (an example is in Fig. 1) for a system formed by a mixture of 1:1 by weight of isotactic polystyrene and of a styrene-*p*-methylstyrene copolymer (30 mole-% *p*-methylstyrene). The presence of two different bands, characteristic of the polystyrene copolymer lattices, is observed in the spectrum of a mechanical mixture of the aforesaid solid polymers. But for the same mixture, after melting at 250–260°, carried on for 10 hr., and after recrystallization treatment (heating at 180° for 2 hr.), the spectrum showed a single band, intermediate between the two previous ones; this indicates the presence of a crystalline lattice having constants intermediate among those of the starting macromolecules.

For the same confusion and crystallization conditions, we did not observe the presence of solid solutions in mixtures of homopolymers such as isotactic polystyrene with isotactic poly-*p*-methylstyrene (20%), with isotactic poly-*p*-chlorostyrene (12%), and with crystalline poly-*p*-fluorostyrene (20%).

(2) Isomorphism of Monomeric Units

This new and interesting case of isomorphism occurs when copolymerizing stereospecifically monomers having a chemical nature, structure, and size that are little different one among the other. We observed cases of this type of isomorphism in products obtained by copolymerization of styrene with many different nuclear-substituted styrenes. These copolymerizations have been carried out with stereospecific catalytic systems, obtained by reaction between titanium halides and organic aluminum compounds, under the same conditions in which styrene and substituted styrenes furnish isotactic polymers.⁵

It is important to point out that, in all the copolymerization systems examined by us, the (r_1r_2) product of reactivity ratios was practically unity. As is known,⁶ this indicates that copolymerization follows the rules of the so-called "ideal" copolymerization, since the two monomers, in the growing chain process, do not show any particular bent either for alternation or for repetition, thus giving origin to macromolecules with a random distribution of the two monomeric units.

Furthermore, all the products examined were obtained by copolymerizations performed until a very limited conversion yield (lower than 5%) was obtained. In this case, independently of remarkable reactivity differences which may exist between the two comonomers the composition of the single macromolecules must not differ remarkably from the mean composition of the copolymer.

Isomorphism of monomeric units was observed by us in different copolymeric systems, for intervals of compositions which may be either complete or more or less limited.

Three different cases of isomorphism of monomeric units may be observed. In fact, the phenomenon appears when: (a) both monomers furnish crystalline homopolymers having the same type of crystalline structure and about the same lattice constants, (b) both homopolymers are crystalline, but with different crystalline structures, and (c) just one of the two homopolymers shows a crystalline stable form.

The second case consists of a particular type of isomorphism which, in analogy with what is observed in solid solutions of low molecular weight substances of different structures, may be defined as "isodimorphism." In fact, the crystals of each homopolymer, corresponding to the stable phase of the other, may be considered as unstable. Also the third case may be considered as a particular case of isodimorphism, if we consider the crystalline phase of one of the homopolymers in the pure state as unstable.

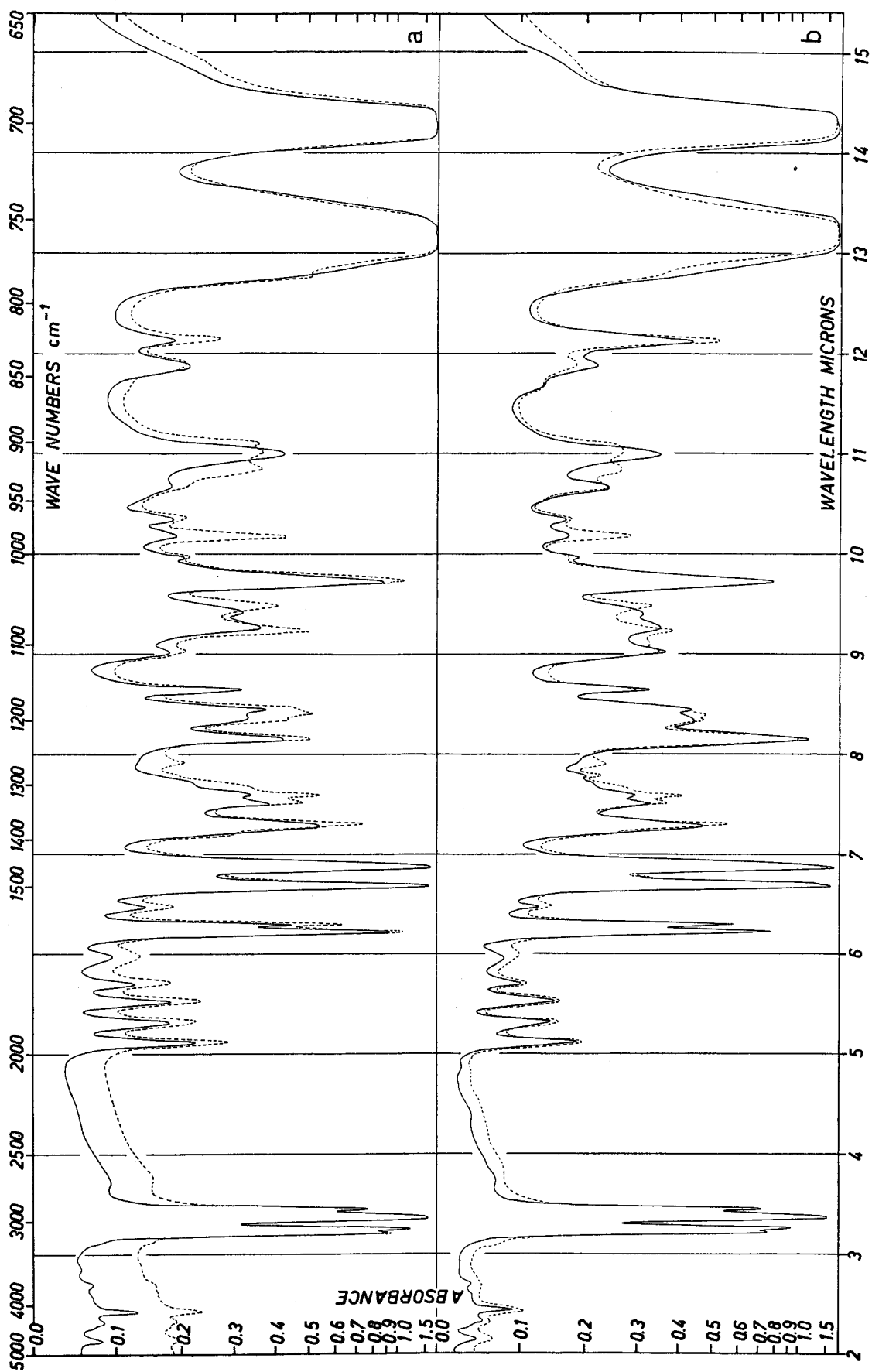


Fig. 2. IR spectra of crystallizable styrene-*o*-fluorostyrene copolymers with a molar content of (a) 5.2% and (b) 16.4% of *o*-fluorostyrene, before (—) and after (---) annealing (2 hr. at 180°C.). The intensity of IR crystallinity bands of polystyrene² decreases with increasing content of comonomeric units.

(a) *Crystalline Copolymers of Monomeric Units Whose Homopolymers Show the Same Type of Crystalline Structure*

The styrene-*o*-fluorostyrene copolymers appear to be crystalline from x-ray examination for the complete set of compositions. They show the same crystalline structure and unvaried lattice constants in the direction of the chains axis with slight variations in the perpendicular directions. By varying the mole content of the two different monomeric units, continuous and regular variations of some physical properties of the copolymer are observed, such as the melting temperature, which ranges from 235° (polystyrene) to 270° (poly-*o*-fluorostyrene).

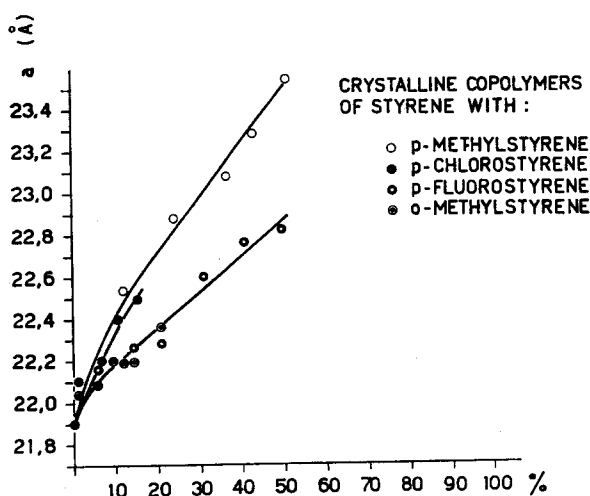


Fig. 3. Variation of the a constant of isotactic polystyrene as a function of the content of copolymerized units of differently substituted styrenes. Abscissa: molar fraction of $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{R}$.

This case of isomorphism for all monomer ratios is possible owing to the same identity period of the two homopolymers (6.63 Å), to the slight difference existing between the sizes of fluorine and of hydrogen, and to the position of fluorine, which replaces a hydrogen atom at a point at which there are no van der Waals' critical contact distances with neighboring atoms.⁷ These are the reasons why each of the two different units following each other along the chain and having the same steric configuration may be indifferently substituted with the other in the same lattice site; this substitution will cause only small variations of the lattice constants in directions normal to the chain axis.

In the IR absorption spectra of these copolymers, on the contrary, a rapid decrease of the crystallinity bands was observed, with an increase in content of each component (Fig. 2). The practical disappearance of the IR crystallinity takes place for compositions varying from about 30% to 70% of a component; this agrees with what can be foreseen for a random distribution of two monomeric units along single threefold helices.

(b) *Crystalline Copolymers of Monomeric Units Whose Homopolymers Show Different Crystalline Structures*

With regard to isotactic homopolymers of styrene and of *p*-fluorostyrene, their stable crystalline modifications show different symmetries. The copolymers obtained from them are crystalline for the whole range of compositions. The copolymers richer in styrene have the structure of the stable form of isotactic polystyrene (threefold helix); those richer in *p*-fluorostyrene have, on the contrary, a crystalline structure corresponding to the stable form of isotactic poly-*p*-fluorostyrene (fourfold helix).⁸ For this case of isodimorphism, it was observed that the addition, in the chain, of monomeric units of even slightly larger size (*p*-fluorostyrene in the polystyrene chain) always causes a remarkable deformation of the lattice constants (Fig. 3). This phenomenon does not take place, on the contrary, in the opposite case, that is, when introducing into the chain a limited number of monomeric units of smaller size (styrene in the chain of *p*-fluorostyrene).

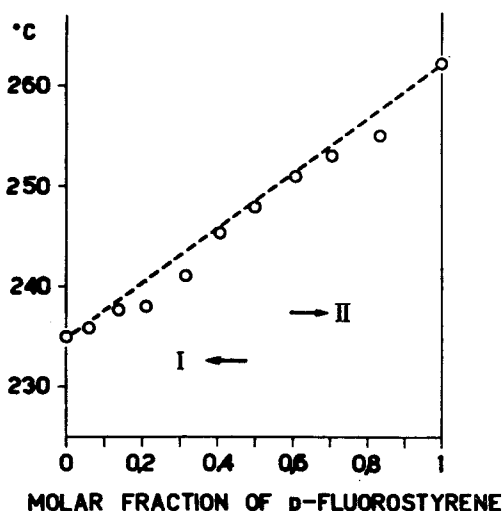


Fig. 4. Melting temperature of crystalline styrene-*p*-fluorostyrene copolymers: (I) crystallites with threefold helix; (II) crystallites with fourfold helix.

The melting temperatures of the crystalline styrene-*p*-fluorostyrene copolymers vary with composition in a linear way between those of the two homopolymers (Fig. 4). Particular discontinuities are not observed in this variation when, for a given intermediate composition, two crystalline phases of different symmetries may be present at the same time.

(c) *Crystalline Copolymers of Monomeric Units with Only One among Them Furnishing Stable Crystalline Homopolymers*

The third case of isomorphism has been observed in a great number of copolymeric systems containing styrene and another monomer giving, by stereospecific polymerization, a homopolymer having an isotactic structure without being crystallizable.⁹ Introduction of different monomeric units

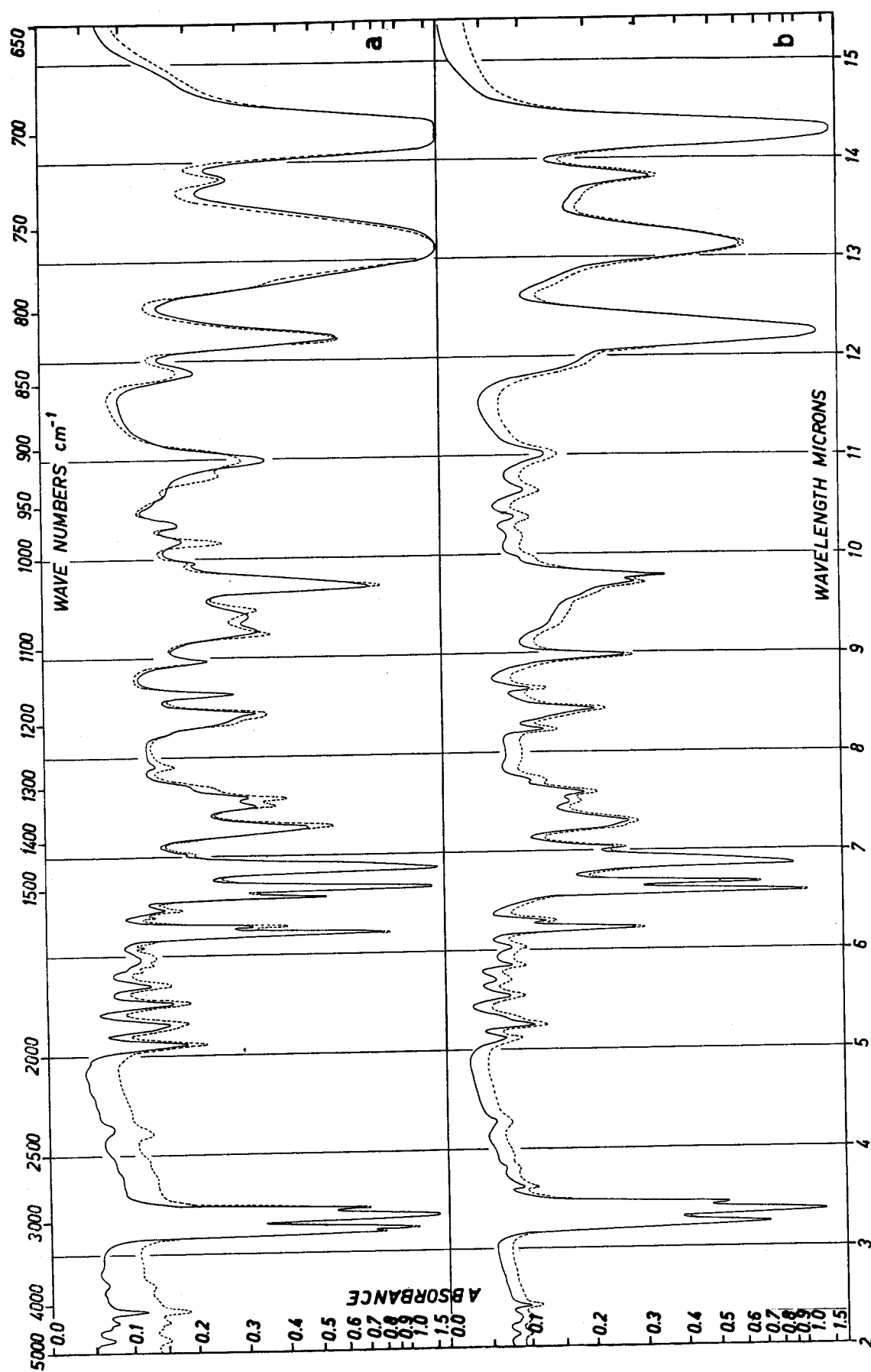


Fig. 5. IR spectra of crystallizable styrene-*p*-methylstyrene copolymers with a molar content of (a) 10% and (b) 51% of *p*-methylstyrene before (—) and after (---) annealing (2 hr. at 180°C.). The IR crystallinity bands of polystyrene disappear in sample b with a molar content of comonomer of about 50%.

does not alter the identity period, but it remarkably modifies the unit cell constants of isotactic polystyrene in the directions of the a and b axes (Fig. 3). These increase regularly with increase in comonomer content; and, the molar composition being equal, the expansion of the unit cell is the more remarkable the larger the steric requirement of the monomeric unit introduced.

In considering isotactic styrene-1-vinylnaphthalene copolymers, it has been observed that the cocrystallization of the copolymer is hindered for vinylnaphthalene contents lower than about 5% on a molar basis; on the contrary, p -ethylstyrene and p -bromostyrene may be placed in the lattice in larger quantity (up to 10–15 mole-%).

The limit contents for which crystallization of the copolymer is still possible in the typical lattice of polystyrene increase remarkably when reducing the size of the bigger comonomer. Thus, crystallizable copolymers containing as much as 30 mole-% of p -chlorostyrene and more than 50% of p -methylstyrene were obtained. In these copolymers, the lattice of the crystalline polystyrene was subjected to an elongation of the a and b axes superior to 2.5 Å., which corresponds to a deformation stronger than 10% in comparison to the starting dimensions.

Besides these composition limits, arrangement of the comonomer molecules in the styrene crystalline lattice becomes impossible and the copolymer appears amorphous by x-rays.

In accordance with what can be foreseen, in all these copolymeric systems IR crystallinity is observed only when the comonomer content is lower than about 30 mole-% (Fig. 5).

MELTING TEMPERATURE OF THE COPOLYMERS

The melting temperatures of the copolymers of isomorphous monomeric units are in general linearly included between those of the corresponding homopolymers when they are both crystalline and show the same symmetry. Generally, also, copolymers of isodimorphous monomeric units behave in a similar way, but in this case hypothetical melting temperatures of the unstable crystalline modifications should be considered.

Also in the case of limited isomorphism phenomena in which a crystalline stable modification of one of the homopolymers is not known, the melting temperature should range from that of the crystalline homopolymer (e.g., isotactic polystyrene) to the hypothetical one which should be peculiar of the other homopolymer if it should crystallize to a lattice having the same symmetry as polystyrene. As a consequence, in some cases the melting temperature of copolymers is increased in comparison with the melting temperature of polystyrene (for example, copolymers with p -chlorostyrene), whereas in other cases (for example, copolymers with p -methylstyrene) it slowly and regularly decreases (Table I). It must be observed that, if isomorphism between the two monomeric units does not take place, the melting temperature of all these copolymers should rapidly decrease, in accordance with the Flory formula.

Fig. 5. IR spectra of crystallizable styrene- p -methylstyrene copolymers with a molar content of (a) 10% and (b) 51% of p -methylstyrene before (—) and after (---) annealing (2 hr. at 180°C.) The IR crystallinity bands of polystyrene disappear in sample b with a molar content of comonomer of about 50%.

TABLE I
Melting Temperatures of Isotactic Copolymers of Styrene
with Differently Substituted Styrenes

Substituted styrene	Molar fraction subst. styrene in copolymer	Cryst. melting temp., °C. ($\pm 2^\circ$)
<i>p</i> -Methylstyrene	0	235
	0.11	227
	0.23	224
	0.335	220
	0.415	212
	0.51	210
	0.65	203
<i>p</i> -Chlorostyrene	0.05	240
	0.075	246
	0.105	248
<i>p</i> -Ethylstyrene	0.10	228
	0.155	226
	0.19	223

From this formula, the melting enthalpy of isotactic polystyrene being 2000–2200 cal./monomeric unit,¹⁰ a content of about 15 mole-% of comonomer should be enough to lower the copolymer melting temperature below 200°. Nevertheless, under these conditions polymer crystallinity also should be remarkably lowered, whereas variations of the lattice constants of crystalline polystyrene should not take place.

COPOLYMERS OF STYRENE WITH NONISOMORPHOUS MONOMERIC UNITS

Unlike the cases described above, noncrystallizable copolymers have been obtained for almost all the composition ranges, copolymerizing styrene and *m*-methylstyrene stereospecifically. This result may be considered in connection with the fact that *m*-methylstyrene gives an isotactic polymer which, owing to a particular steric effect of the methyl group in the *meta* position, crystallizes to a structure that is more complex than the one usually observed (helix type, 11₃; identity period, 21.74 Å).¹¹

It must be remembered that one of the critical van der Waals' contact distances in the determination of the lattice constants of crystalline polystyrene is caused by hydrogen in a *meta* position which approaches the *m*-hydrogen atom of the neighboring molecule at the least possible distance. We can therefore conclude that, in order that isomorphism among monomeric units may take place, it is necessary not only that the monomers polymerize and copolymerize with the same mechanism, but also that the corresponding monomeric units do not exhibit different steric requirements, while still considering the critical van der Waals' contact distances.

Only under these conditions may they copolymerize, keeping in the chain the same identity period or a very similar one to that observed along the chain of one of the two homopolymers, without excessive deformations of the other lattice constants.

AMORPHOUS ISOTACTIC POLYMERS AND COPOLYMERS

The lack of crystallinity observed by x-rays in some of the copolymers examined is clearly due only to the inability of some monomeric units to arrange themselves in a crystalline lattice of another, owing to the steric hindrance of the lateral groups.

In some cases, in fact, it may be demonstrated that it is not the presence of steric or structural chain irregularities that hinders crystallization. For instance, when an amorphous styrene-*p*-chlorostyrene (1:1 in moles) copolymer was subjected to hydrogenation with dehalogenation, at 200° with nickel Raney catalyst at 180 atm. of H₂, crystalline isotactic polyvinylcyclohexane was obtained. Furthermore, hydrogenating, under the same conditions, samples of amorphous copolymers of styrene with more than the 50% of *p*-methylstyrene, yielded crystalline products. In this case the hydrogenation, transforming the tolyl into methylcyclohexyl groups, decreases the ratio of length to thickness of the lateral substituents, thus allowing a better packing of the isotactic chains in the lattice. It follows that, whereas *p*-methylstyrene and styrene are not capable of complete isomorphous substitution, the presence of monomeric units deriving from vinylcyclohexane and from vinylmethylcyclohexane does not hinder crystallization of the hydrogenated copolymer.

The rules determining isomorphism among monomeric units appear less simple than those known for the inorganic compounds, in particular for compound of ionic nature. In fact, whereas for bivalent or trivalent metallic ions isomorphism depends on the radius, and therefore on the volume of the ion, in the case of isomorphism among monomeric units a great closeness of the molecular volumes is, though necessary, not sufficient to determine isomorphism. Thus, from the examples given above it appears that the monomeric unit of styrene is isomorphous with *p*-methylstyrene, though not with *m*-methylstyrene.

It follows that a factor determining isomorphism among monomeric units is the shape in relation to the characteristic contact distances existing between the atoms in the crystalline lattice.

A monomeric unit with a volume a little different from that of another unit may be nonisomorphous if its shape leads to highly improbable van der Waals' contact distances. But when the increased size of the monomeric units is employed mostly to fill the empty spaces existing in the lattice, isomorphism is possible for remarkable differences in the volumes of the copolymerized monomeric units.

References

1. Natta, G., *Makromol. Chem.*, **35**, 94 (1960).
2. Morero, D., E. Mantica, F. Ciampelli, and D. Sianesi, *Nuovo Cimento Suppl.*, **15**, 122 (1960).
3. Natta, G., and P. Corradini, *Nuovo Cimento Suppl.*, **15**, 40 (1960). Natta, G., P. Corradini, and I. W. Bassi, *ibid.*, 52, 68.
4. Natta, G., M. Farina, and M. Peraldo, *Atti accad. nazl. Lincei, Rend., Classe sci. fis. mat. e nat.*, **25**, 424 (1958). Peraldo, M., and M. Farina, *Chimica e industria Milan*, **42**, 1350 (1960).
5. Natta, G., F. Danusso, and D. Sianesi, *Makromol. Chem.*, **30**, 238 (1959). Sianesi, D., G. Pajaro, and F. Danusso, *Chimica e industria Milan*, **41**, 1176, (1959).
6. See, for example, Alfrey, T., J. Bohrer, and H. Mark, *Copolymerization*, Interscience, New York-London, 1952, p. 136.
7. Natta, G., P. Corradini, and I. W. Bassi, *Nuovo Cimento Suppl.*, **15**, 83 (1960).
8. Natta, G., P. Corradini, and I. W. Bassi, *Gazz. chim. ital.*, **89**, 784 (1959); *Angew. Chem.*, **70**, 598 (1958).
9. Natta, G., and D. Sianesi, *Atti accad. nazl. Lincei, Rend., Classe sci. fis. mat. e nat.*, **26**, 418 (1959).
10. Danusso, F., and G. Moraglio, *ibid.*, **27**, 382 (1959).
11. Corradini, P., and P. Ganis, *J. Polymer Sci.*, **43**, 311 (1960).

Synopsis

Through x-ray and infrared examinations of stereoregular polymers and copolymers of vinylaromatic monomers, the occurrence of chain isomorphism phenomena, together with many cases of a new type of isomorphism between monomeric units, have been proved. Isomorphism of macromolecules, allowing true solid solutions, has been observed when melting and crystallizing mixtures of homopolymers (i.e., isotactic polystyrene) and of crystalline copolymers (i.e., styrene-*p*-methylstyrene) having the same identity period and differing very little in lattice constants. Isomorphism among monomeric units occurs in copolymerizing monomers that have a chemical nature and shape slightly different one from the other, e.g., styrene and *o*-fluorostyrene. This allows the formation of crystallizable copolymers in the entire composition range. They show physical properties (lattice constants, melting temperatures, etc.) continuously varying between those of the pure homopolymers. The occurrence of isodimorphism phenomena has been observed in crystalline copolymers obtained from monomers the homopolymers of which have different crystalline structures (e.g., styrene-*p*-fluorostyrene), and also in copolymerizing styrene with monomers (e.g., *p*-methyl, *p*-chlorostyrene) giving only amorphous homopolymers. In the latter case, of course, the copolymers show crystallinity only in a limited composition range.

Résumé

Par examen aux rayons-X et par examen à l'I.R. des polymères stéréoréguliers, et des copolymères des monomères vinyliques aromatiques, on a prouvé qu'il se passe un phénomène d'isomorphisme dans la chaîne ainsi que d'autres cas d'un nouveau type d'isomorphisme au sein des unités monomériques. L'isomorphisme des macromolécules, en permettant des vraies solutions solides, a été observé lorsqu'on cristallise des mélanges d'homopolymères (par ex. polystyrène isotactique) et de copolymères (par. ex. styrène, *p*-méthylstyrène) qui ont le même motif périodique et ne diffèrent que très peu du point de vue des constantes du réseau. L'isomorphisme au sein des unités monomériques se présente lorsqu'on copolymérise des monomères qui ont une nature chimique et des conformations qui ne diffèrent que très peu entr'elles, comme le styrène et l'*ortho*-fluorostyrène. Cela permet une formation de copolymères cristallisables dans tout l'intervalle de composition. Ils montrent des propriétés physiques (par ex. constantes

du réseau, température de fusion) qui varient continuellement entre celles des homopolymères. Les phénomènes d'isomorphisme ont été observés dans les copolymères cristallins obtenus à partir de monomères dont les homopolymères ont une structure cristalline différente (par ex. styrène, *para*-fluorostyrène) de même qu'en copolymérisant le styrène avec des monomères (par ex. *para*-méthyl, *para*-chlorostyrène) qui donnent seulement des homopolymères amorphes. Dans ce dernier cas, naturellement, les copolymères montrent une cristallinité uniquement dans un intervalle de composition limitée.

Zusammenfassung

Röntgenstrahl- und Infrarotuntersuchungen an sterisch geordneten Polymeren und Copolymeren von vinylaromatischen Monomeren haben das Auftreten der Erscheinung der Kettenisomorphie, neben zahlreichen anderen Typen der Isomorphie zwischen Monomereinheiten bewiesen. Isomorphie bei Makromolekeln ermöglicht die Ausbildung echter fester Lösungen; diese Erscheinung wurde beim Aufschmelzen und Kristallisieren von Gemischen von Homopolymeren (z.B. isotaktisches Polystyrol) und kristallinen Copolymeren (z.B. Styrol/*p*-Methylstyrol), die gleiche Identitätsperiode besitzen und deren Gitterkonstanten sich nur sehr wenig voneinander unterscheiden, beobachtet. Isomorphie zwischen Monomereinheiten tritt auf, wenn man Monomere, deren chemische Natur und Form sich nur wenig voneinander unterscheiden (z.B. Styrol und *o*-Fluorstyrol), copolymerisiert. Dies gestattet die Gewinnung von kristallisierbaren Copolymeren im gesamten Zusammensetzungsbereich. Die physikalischen Eigenschaften (z.B. Gitterkonstanten, Schmelztemperaturen) gehen kontinuierlich von denen des einen in die des anderen Homopolymeren über. Das Auftreten von Isomorphie-Phänomenen wurde in kristallinen Copolymeren, die man aus Monomeren erhält, deren Homopolymere verschiedene Kristallstruktur besitzen (z.B. Styrol/*p*-Fluorstyrol) sowie bei der Copolymerisation von Styrol mit Monomeren (z.B. *p*-Methyl-, *p*-Chlorstyrol), die nur amorphe Homopolymere liefern, beobachtet. Im letzteren Fall zeigt das Copolymere Kristallinität natürlich nur in einem begrenzten Zusammensetzungsbereich.

Received February 15, 1961