

X-Ray Study of Some Isotactic Substituted Poly-Carboalkoxybutadienes

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Synopsis

The chain conformation and configuration of some polysorbates and poly- β -styrylacrylates is discussed in this paper. From x-ray fiber spectra of these polymers we obtained the identity period of 4.80 ± 0.05 Å. The conformation of the main chain is the same as that of 1,4 *trans* polybutadiene and isotactic 1-4 *trans* polypentadiene. From considerations of the mode of packing of the chains and of the encumbrance of the side groups in respect to the main chain it was possible to assign an *erythro* configuration in regard to the relative placement of lateral groups. The examined polymers are tri-tactic and have a *trans-erythro*-isotactic configuration.

A new series of crystalline polymers has been obtained at the Department of Industrial Chemistry of the Polytechnic of Milan by Natta and Farina¹ starting from substituted carboalkoxybutadienes. In particular, crystalline polymers have been obtained from various alkyl esters of the *trans-trans* isomer of sorbic acid and β -styrylacrylic acid. The monomer units with 1,4 enchainment are of the type $-\text{CHR}-\text{CH}=\text{CH}-\text{CHCOOR}'-$. They show three sites of possible stereoisomerism, i.e., the double bond and the two tertiary carbon atoms of the chain. In this paper we shall report the results of an x-ray analysis of these polymers. Some of the corresponding preliminary results have been reported previously.²

X-Ray Data

The powder spectra of five typical polymers recorded with a Geiger counter are shown in Figure 1. From the fiber spectra of all polysorbates and of the poly(β -styryl *n*-butylacrylate) we obtained the same value of the identity period along the fiber axis, i.e., $c = 4.80 \pm 0.05$ Å. The spacings of the two most intense equatorial reflections are shown in Table I.

The spacing of the first line varies regularly with an increase in the encumbrance of the lateral group; the spacing of the second line is about the same for all the polymers studied.

The reconstruction of the reciprocal lattice has been possible for the equatorial reflections of poly(*n*-butyl sorbate); the reciprocal axes, which

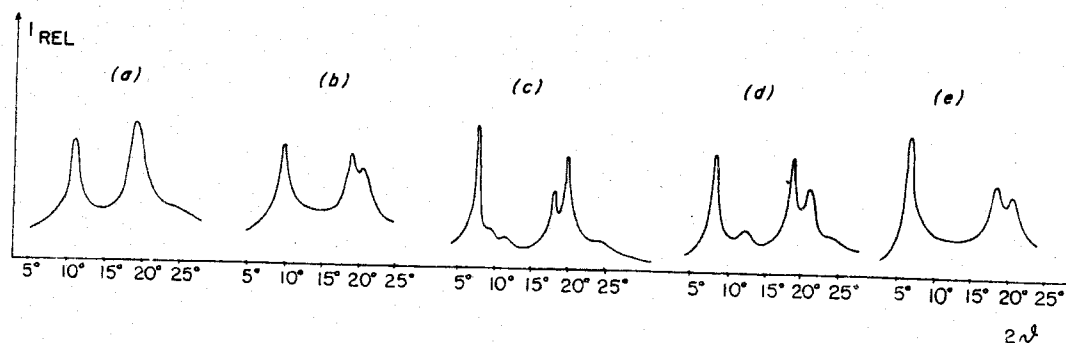


Fig. 1. Powder spectra ($\text{CuK}\alpha$) of the crystalline polymers: (a) poly(methyl sorbate); (b) poly(ethyl sorbate); (c) poly(*n*-butyl sorbate); (d) poly(methyl- β -styrylacrylate); (e) poly(*n*-butyl- β -styrylacrylate).

are perpendicular to each other are: $a^* = 1/(11.36 \pm 0.10) \text{ \AA}^{-1}$; $b^* = 1/(9.70 \pm 0.10) \text{ \AA}^{-1}$. On the first layer line only four reflections are observed; therefore no complete reconstruction of the reciprocal lattice has been attempted.

TABLE I

| | 2θ ($\text{CuK}\alpha$) | $d, \text{ \AA}$. | 2θ ($\text{CuK}\alpha$) | $d, \text{ \AA}$. |
|--|-------------------------------------|--------------------|-------------------------------------|--------------------|
| Poly(methyl sorbate) | 10.95 | 8.07 ± 0.10 | 19.00 | 4.67 ± 0.05 |
| Poly(ethyl sorbate) | 9.90 | 9.90 ± 0.10 | 19.00 | 4.67 ± 0.05 |
| Poly(isopropyl sorbate) | 8.40 | 10.52 ± 0.10 | 18.80 | 4.71 ± 0.05 |
| Poly(<i>n</i> -butyl sorbate) | 7.75 | 11.40 ± 0.10 | 18.10 | 4.92 ± 0.05 |
| Poly(isobutyl sorbate) | 7.40 | 11.94 ± 0.10 | 19.40 | 4.57 ± 0.05 |
| Poly(isoamyl sorbate) | 6.80 | 12.99 ± 0.10 | 18.10 | 4.92 ± 0.05 |
| Poly(methyl- β styrylacrylate) | 7.60 | 11.62 ± 0.10 | 18.30 | 4.83 ± 0.05 |
| Poly(<i>n</i> -butyl- β styrylacrylate) | 6.25 | 14.00 ± 0.15 | 18.10 | 4.92 ± 0.05 |

Possible Configurational Models

Each chain should be ordered in respect to the three centers of stereoisomerism, at least for long sequences of monomeric units. In fact, the x-ray crystallinity is high, and the infrared spectrum of the polymer in the solid state is very different from the corresponding spectrum of the melt.

Accordingly, at least for long sequences of monomeric units, we shall expect the following regularities: (1) the double bond must be always of the *cis* or always of the *trans* type; (2) the relative configuration of successive monomeric units must be either isotactic or syndiotactic; (3) the relative configuration of two adjacent tetrahedral centers of stereoisomerism must be either of the *threo* or of the *erythro* type.

The possible configurational models are shown in Figure 2.

Chain Conformation

The identity period along the fiber axis is identical to that found for 1,4-*trans*-polybutadiene.³ The identity unit contains only one monomer unit, as shown by the equatorial dimensions found for poly(*n*-butyl sor-

bate) and by the distribution of diffracted intensity on the meridian of the successive layer lines.

Accordingly, the chain conformation should be characterized by a succession of internal rotation angles very close to the sequence:...*trans*, $\sigma_1 = 120^\circ$, $\sigma_2 = 180^\circ$, $\sigma_3 = -120^\circ$, *trans*... (Fig. 3). The assignment of a *trans* configuration to the double bonds is confirmed by the appearance in the infrared spectra, of a band at 10.52μ .

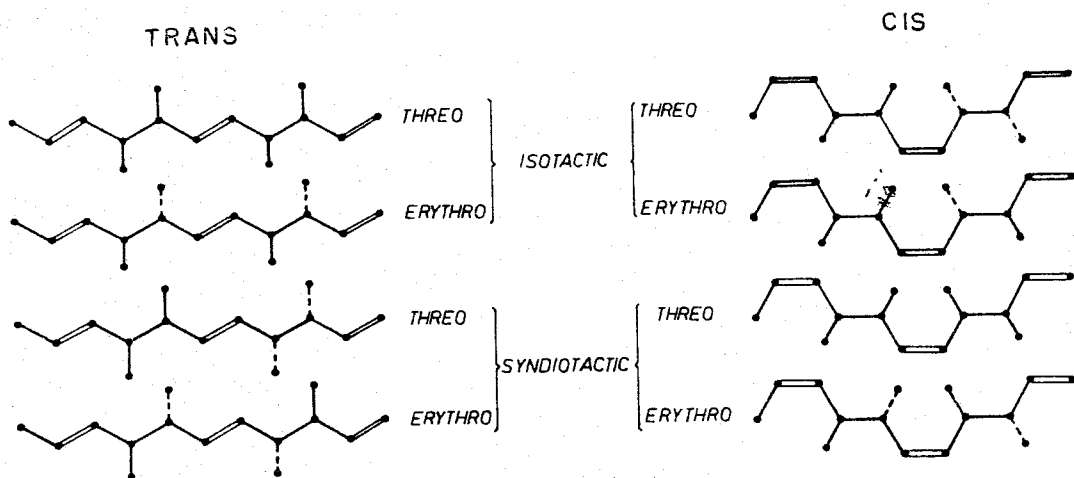


Fig. 2. Possible configurational models of the examined polymers.

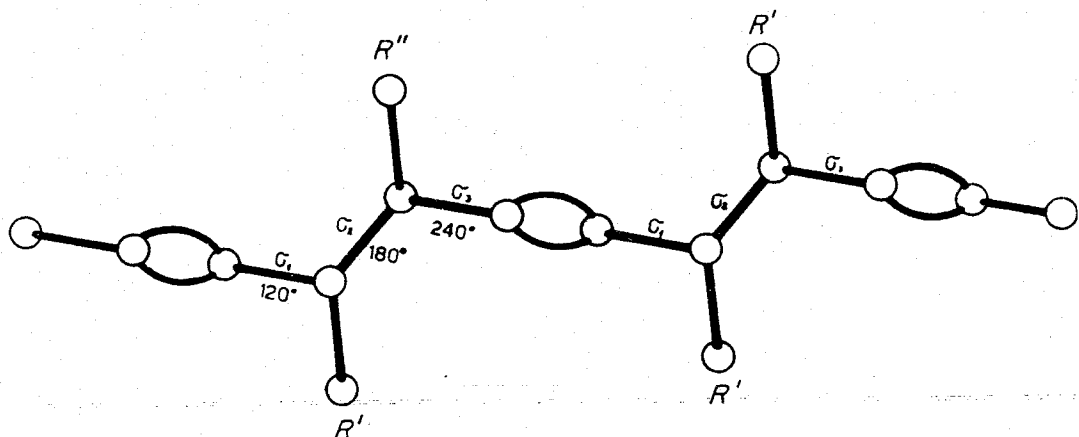


Fig. 3. Chain conformation of the examined polymers. $R' = \text{CH}_3, \text{C}_6\text{H}_5$; $R'' = -\text{COOR}$.

Moreover, the successive monomeric units must necessarily be of the isotactic type. Thus, for the examined polymers, the knowledge of the identity period along the fiber axis and very simple considerations on the intensity distribution are sufficient to permit the type of tacticity of two of the centers of stereoisomerism to be assigned with certainty. The situation is analogous to that of ditactic polymers such as poly-1,4-*trans*-penta-diene.⁴

A qualitative model of the packing of the macromolecules is shown in Figure 4 for poly(*n*-butyl sorbate). We have assumed a plane group *pg*, owing to the fact that the a^* and b^* axes are perpendicular to each other.

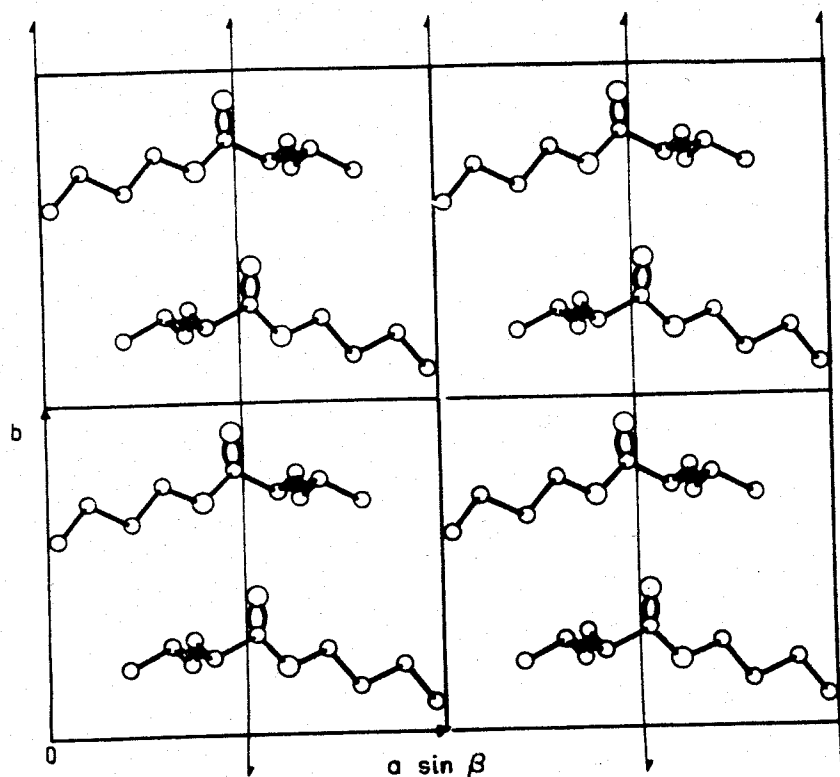


Fig. 4. Qualitative packing model of poly(*n*-butyl sorbate).

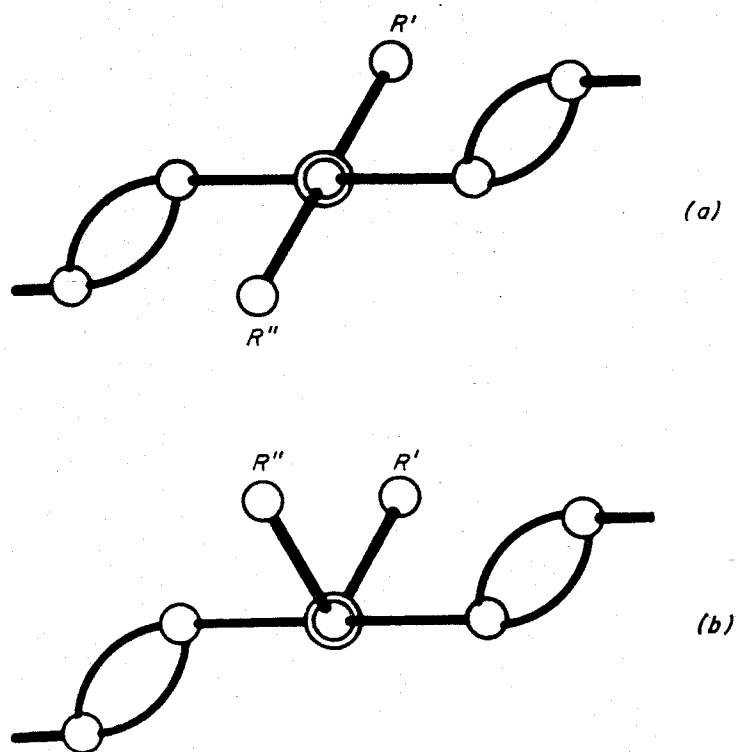


Fig. 5. Models of (a) *erythro* configuration of two tertiary carbon atoms, the lateral groups having a *trans* arrangement; (b) *threo* configuration with a *gauche* arrangement of the lateral groups.

The plane group pm may be discarded on the basis of elementary considerations on the intensity of the reflections.

Since the space group was unknown, this model was regarded as a first approximation and therefore was not refined further, though there was reasonable agreement between calculated and observed structure factors.

The mode of packing of the chains for the other polymers should be in some way similar to that of poly(*n*-butyl sorbate), with chain packing side by side, with parallel orientation of the direction of maximum encumbrance. This is in agreement with the main features of the equatorial spectra of all the investigated polymers.

As already remarked, the spacing of one of the two strongest equatorial reflections varies regularly with an increase of the bulkiness of the side groups; accordingly it arises from planes perpendicular to the direction of maximum encumbrance. The spacing of the other strong equatorial reflection is almost invariant in the polymer series studied; thus it should arise from planes nearly parallel to the direction of maximum encumbrance.

The fact that the equatorial encumbrance of the chains varies practically only in one direction points to a *trans* arrangement, and hence to an *erythro* placement of the lateral groups (Fig. 5).

Further Considerations on Poly(β -styryl Acrylates)

Although it was not possible to obtain oriented fibers of poly(methyl- β styrylacrylate), oriented crystalline fibers were obtained in the case of poly(*n*-butyl- β -styrylacrylate).

The main features of the spectrum are very similar to those of the various studied polysorbates. However, for the polysorbates polymers, some doubt could remain about a possible *gauche* (instead of *trans*) placement of the methyl group with respect to the carboxylic group, but it is impossible to build a stereochemically reasonable model of the chain of poly(*n*-butyl- β -styrylacrylate) with a *gauche* arrangement of the benzene and carboxylic group (Fig. 6).

This fact is strongly indicative of an *erythro* isotactic configuration of the polymer. Simple calculations of the internal conformation energy for a *threo* and an *erythro* configuration of the side group associated with the known conformation of the chain gives rise for poly(*n*-butyl- β -styrylacrylate) to a very large internal energy difference.

A *trans* conformational arrangement (and hence an *erythro* placement) of the side groups is indicated also by the nuclear magnetic resonance spectra, which have been recorded for all the studied polymers.⁶

Conclusions

The examination of the x-ray spectra of some polysorbates and poly(β -styrylacrylates) allows a unequivocal assignment of a *trans*-isotactic configuration to the studied polymers. From considerations on the mode

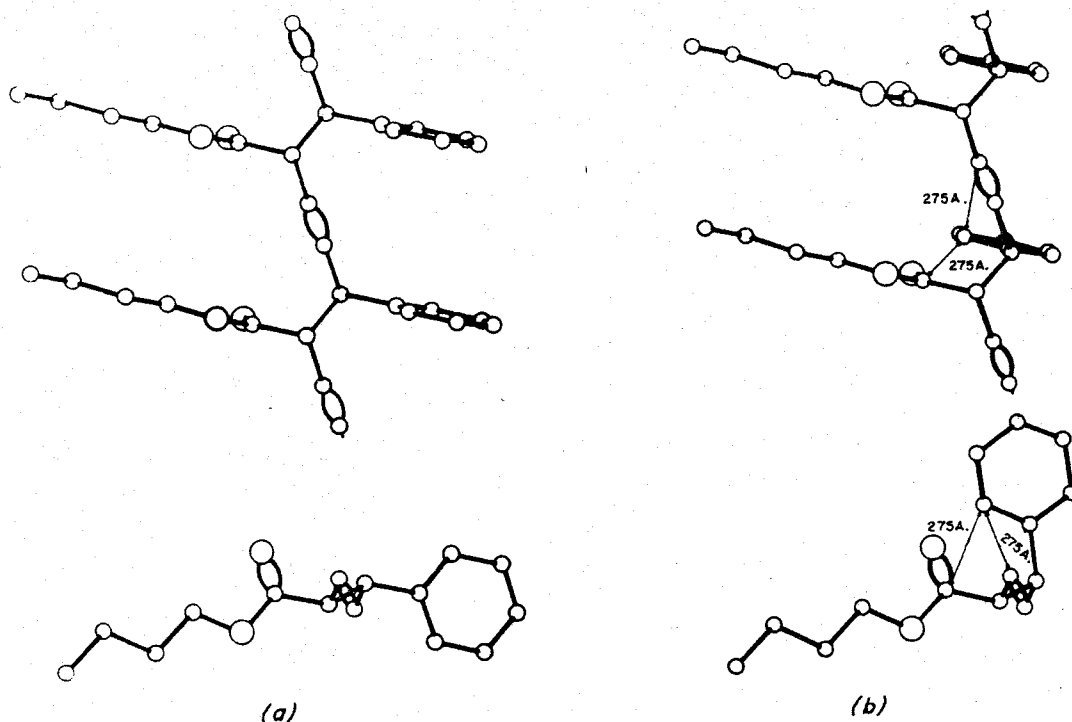


Fig. 6. Chain models of poly(*n*-butyl- β -styrylacrylate): (a) with a *trans* arrangement of the benzene and carboxylic group (*erythro* configuration); (b) with a *gauche* arrangement of the benzene and carboxylic group (*threo* configuration); in this case the worst intramolecular atomic distances are shown.

of packing of the chains and on the encumbrance of the side groups as regard to the main chain permits one to assign an *erythro* configuration with respect to the relative placement of lateral groups.

The polymers we have studied are tritactic and have, at least for long sequences of monomeric units, a *trans-erythro-isotactic* configuration.

References

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Résumé

Cet article traite de la conformation et de la configuration de quelques polysorbates et poly- β -styrylacrylates. Ces polymères ont été examinés sous forme de fibres aux rayons-X; on a trouvé la valeur de 4.80 ± 0.05 A. comme longueur du motif périodique. La conformation de la chaîne principale est égale à celle du polybutadiène-1-4-*trans* et du polypentadiène-1-4-*trans* isotactique. En considérant la manière d'empaquettement des chaînes et l'encombrement des groupes latéraux par rapport à la chaîne principale,

il a été possible de déterminer une configuration *érythro* du point de vue de la localisation des groupes latéraux. Les polymères étudiés sont pourtant tritactiques et leur configuration est *trans-érythro*-isotactique.

Zusammenfassung

In der vorliegenden Arbeit wird die Kettenkonformation und Konfiguration einiger Polysorbate und Poly- β -styrylacrylate diskutiert. Das Röntgenfaserdiagramm dieser Polymeren zeigt eine Identitätsperiode von $4,80 \pm 0,05$ Å. Diese Polymeren besitzen daher die gleiche Kettenkonformation wie das 1,4-*trans*-Polybutadien und das isotaktische 1,4-*trans*-Polypentadien. Die relative Stellung der seitlichen Gruppen entspricht einer Erythrokonfiguration, wie durch eine Untersuchung der Kettenpackung und die Hinderung der seitlichen Gruppen in Bezug auf die Hauptkette bewiesen wird. Die Polymeren sind tritaktisch und besitzen eine *trans-érythro*-isotaktische Konfiguration.

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