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Molecular Configuration of Stretched Polyisobutilene*

By A. M. Liquori

Istituto di Chimica Farmaceutica, Università di Roma, and Centro di Strutturistica Chimica del C.N.R., Rome, Italy

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A number of helical configurations for stretched polyisobutilene have been selected on the basis of simple geometrical considerations. A quasi-statistical analysis has been carried out by the use of Crick, Cochran & Vand's recent theory on the Fourier transform of atoms on a helix.

The results indicate that the intensity distribution of the X-ray fibre diagram agrees with that predicted for a uniform helical configuration containing 8/5 monomers per turn and implying a C–C–C angle of about 114° for the backbone chain.

Introduction

From the point of view of the relations between molecular structure and physical properties of high polymers, polyisobutilene is one of the most interesting substances. Although strong repulsions between the methyl groups may be predicted from its chemical constitution, the physical properties call for very flexible molecules. Furthermore, as found by Brill & Halle (1938), this polymer readily crystallizes on stretching, giving an excellent fibre diagram which may be expected to contain all the necessary data for a detailed investigation of its molecular structure.

Brill & Halle proposed the following orthorhombic unit cell:

$$a = 6{\cdot}94,\ b = 11{\cdot}96,\ c = 18{\cdot}63\ \text{Å}\ ,$$

and concluded from the unusually high value of the fibre period c that the molecules probably have a spiral structure.

Fuller, Frosch & Pape (1940) were able to index all the diffraction spots contained in the X-ray diagram and showed the presence of a sub-periodicity of 2·33 Å = $c/8$ along the fibre axis. From the unit-cell dimensions and from the density, these authors deduced that two molecular chains, each consisting of eight monomers, are contained in the unit cell. They proposed a spiral structure which arises when a planar zigzag molecule is rotated consistently in the same direction around every C–C bond of the backbone chain. This configuration was not proved by calculations of the diffraction intensities, but was essentially based upon the agreement between the observed monomer repeat of 2·33 Å and the monomer repeat calculated for this structure, assuming C–C distances of 1·54 Å and C–C–C angles of 109°.

The present investigation, carried out on completely different lines, has led to a configuration which differs from that proposed by Fuller *et al.*, and is in general agreement with the intensity distribution of the X-ray diagram.

Allowed helical configurations for polyisobutilene

The whole procedure was based on the assumption of a helical configuration, and not on trials by using fixed models. If no other restrictions are used, it is obvious that many helical configurations can be obtained with the same monomer repeat, 2·33 Å. These configurations are distinguished by the number of turns contained in one identity period c = 18·63 Å, and therefore by the axial distances P between two successive turns.

The number of possible configurations is limited by the fact that an even number of monomers, namely 8, is contained in the identity period c. Therefore, a helical configuration must make an odd number of turns in order not to generate a smaller unit cell.* Furthermore, since the number of turns must be less than the number of monomers, only four general types of helical configurations are possible (Table 1).

Table 1

Configuration	Monomer repeat, p	Number of turns in the fibre period c	Axial distance, P, between successive turns	Monomers per turn
S_1	$c/8$ = 2·33 Å	1	c	8
S_3	$c/8$ = 2·33 Å	3	$c/3$	8/3
S_5	$c/8$ = 2·33 Å	5	$c/5$	8/5
S_7	$c/8$ = 2·33 Å	7	$c/7$	8/7

Only configurations S_5 and S_7 were examined in detail in order to decide which of them agreed with the intensity distribution of the diffraction pattern. Configurations S_1 and S_3 were not considered since helices of the above type, having all the atoms of the

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* Paper read at the Thirteenth International Congress of Pure and Applied Chemistry, Stockholm 1953.

* A helical configuration with an even number of monomers making an even number of turns in the identity period c would still be possible if a reversal of direction of the helix after each complete rotation could be assumed. This can be considered to be very unlikely.

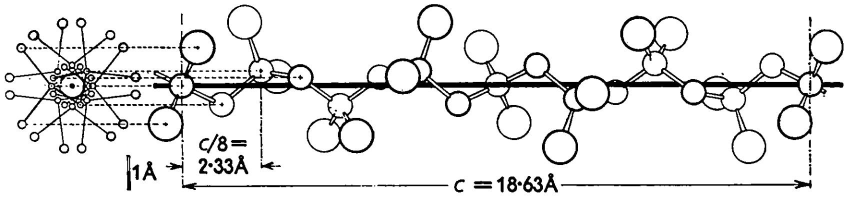

Fig. 1. Drawing of a crystallized polyisobutilene molecule in configuration S_5. The metilene groups of the backbone chain are denoted by smaller spheres, and the methyl groups are denoted by larger spheres.

backbone chain exactly or nearly located on the same spiral, were found not to be stereochemically feasible.

A uniform spiral S_7, based on an axial distance $P = c/7$ and a monomer repeat $p = 2{\cdot}33$ Å, corresponds to that proposed by Fuller *et al.* and implies a C–C–C angle of 109° and a C–C distance of 1·54 Å. A uniform spiral S_5, making five turns in the fibre period and having, therefore, an axial distance between successive turns of $P = c/5$ is shown in Fig. 1. This configuration has the same monomer repeat of 2·33 Å but is obviously different from the preceding one and implies a C–C–C angle of 114°.

This rather large deformation of the bond angle, to which a helical configuration is very sensitive, might explain why such a structure was considered neither by Fuller *et al.* nor by Huggins (1945) in a later general survey of the spiral configuration of stretched polymers. It may be pointed out that a structure very similar to the S_5 was described by Bunn (1947) in a review paper and was considered by him as a very promising alternative to the structure proposed by Fuller *et al.* Confirmatory data were deferred until a later publication, but no further paper has so far been issued.*

Comparison of the model with the X-ray intensity distribution

In order to decide between the two configurations S_5 and S_7 the usual and cumbersome procedure of calculating the intensities by trial and error and comparing them with the observed intensities was replaced by a quasi-statistical criterion based on a recent and very elegant theory of Crick, Cochran & Vand (1952) on the Fourier transform of atoms with a helical arrangement.

Giving cylindrical coordinates R, ψ, l/c to a lattice plane in reciprocal space, instead of cartesian coordinates h, k, l, the intensities diffracted by a lattice containing one helical molecule per lattice point can be calculated from the squares of the following Fourier transform:

$$F(R, \psi, l/c) = \sum_n \sum_j f_j J_n(2\pi R r_j) \exp\,[ni(\psi+\varepsilon_j)]\,, \quad (1)$$

where

$$\varepsilon_j = \pi/2 - \varphi_j + 2\pi l z_j/nc\,,$$

and r_j, φ_j, z_j represent the cylindrical coordinates of the atoms of a monomer.

J_n are Bessel functions, the orders n of which are obtained for reflexions on the lth layer line by solving the equation

$$l/c = n/P + m/p \quad (2)$$

for all integer values of m, positive and negative. P and p are, respectively, the axial distance between two successive monomers and two successive turns of a given helix.

For the configurations S_5 and S_7, P assumes the values of $c/5$ and $c/7$, respectively, while p has the constant value of $c/8 = 2{\cdot}33$ Å. Consequently the following equations apply to the two different configurations:

$$l = 5n + 8m,\quad l = 7n + 8m\,.$$

It will now be observed that within the maximum value of $2\pi R r_j$ as fixed by packing requirements, only low-order Bessel functions make appreciable contributions to the transform, so that the first summation practically ends with the first term. Therefore, only the first solution of equation (2) is of interest.

Under these circumstances, a statistical prediction can be made for the intensity distribution corresponding to the configurations S_5 and S_7 by considering that a strong reflection can occur on a particular layer line of the diffraction pattern only if the corresponding Bessel function is of a low order. Such a condition is not affected by the fact that there are actually two chain molecules in the unit cell of polyisobutilene; the contribution of the second chain to the structure factor is in fact obtained by multiplying the transform (1) by a 'fringe function'.

In Table 2 the orders of Bessel functions corresponding to the two configurations are listed for the successive layers of the fibre diagram. An estimated average intensity is also given. It can be seen that for the configuration S_5 this average intensity is the stronger, the lower the order of n; this checks with theory. A definitive disagreement exists, however, for configuration S_7, which has therefore to be ruled out.

Further and stronger evidence in favour of the configuration S_5 is given in Fig. 2 showing a plot of Bessel functions against $2\pi Rr$. Values of $2\pi R r_j$ for

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* After this paper had been read in Stockholm, Dr Bunn kindly informed me that after having obtained evidence in favour of such a structure, the work was suspended. The problem has been taken up again in Dr Bunn's laboratory in order to analyze it in detail by structure-factor calculations.

Table 2

Index, l, of the layer	Estimated average intensity of the layer	Order, n, of the Bessel function	
		S_5	S_7
0	*vs*	0	0
1	*mw*	3	−1
2	*m*	−2	−2
3	*s*	1	−3
4	*m*	−4	4
5	*s*	−1	3
6	*m*	2	2
7	*w*	−3	1
8	*s*	0	0
9	*vw*	3	−1
10	*w*	−2	−2
11	*mw*	1	−3

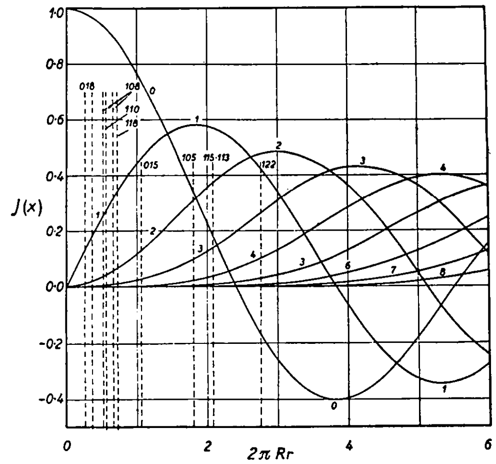

Fig. 2. Plot of Bessel Functions against $2\pi Rr$. The broken lines denoting the values of $2\pi Rr_j$, for the very strong reflexions have an arbitrary height.

configuration S_5 corresponding to reflexions classified as very strong by Fuller *et al.* are indicated by vertical lines. It can be seen that these very intense reflexions always occur in regions of the diffraction pattern where the corresponding Bessel functions assume their maximum values for the configurations S_5.

This agreement confirms the initial assumption of a helical configuration and leaves little doubt that a helix containing 8/5 monomers per turn is the correct configuration for stretched polyisobutilene. Departures from such an ideal structure are likely to be present, and there is actual evidence in the X-ray diagram.

Discussion of the results

It should be emphasized that the results of this investigation afford a very good example of the usefulness of the Fourier transform method for recognizing the presence of helical configurations from a general survey of the X-ray diagram of a chain polymer. Without undertaking a detailed structure determination, this method can give useful information of both chemical and physical interest. In the case of polyisobutilene, a head-to-tail chemical constitution of the polymer has received a clear-cut confirmation by this study. From the point of view of the physical properties, at least two features of the structure are relevant: (*a*) the short distances between the methyl groups, which is clear evidence for the presence of strong intramolecular repulsions; (*b*) the approximately cylindrical symmetry of the crystallized molecules, which favours the pseudo-hexagonal packing. Both these features may aid in interpreting the stress–strain behaviour of this synthetic elastomer.

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