

Complexation of Stereoregular Poly(methyl methacrylates). 14. The Basic Structure of the Stereocomplex of Isotactic and Syndiotactic Poly(methyl methacrylate)

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ABSTRACT: The basic structure of the stereocomplex of isotactic and syndiotactic PMMA was investigated by means of X-ray fiber diffraction. It is shown that the results including a meridional reflection on the ninth layer line can be explained in terms of a 9/1 double-stranded helix, having an asymmetric unit consisting of 1 isotactic unit and 2 syndiotactic units. An apparent 2-fold axis of symmetry is ascribed to the existence of a specific kind of disorder, caused by the fact that there are two ways of intertwining the two chains, related to each other by a rotational angle of about π . The proposed structure appears to be highly tolerant with respect to structural errors such as chain ends, loops, or inferior stereoregular sequences, explaining the fact that even for samples of low tacticity complex is formed. From the proposed structure, it is suggested that the driving force for complexation is a good sterical fit between the two chains, stabilizing each other's energetically most favorable (close to all-trans) conformation.

Introduction

Ever since the first report of Fox et al.¹ 30 years ago, the phenomenon of stereocomplexation between isotactic (it) and syndiotactic (st) PMMA has been the subject of extensive investigations, and the literature on this topic was recently reviewed by Špeváček and Schneider.² However, the basic structure of the complex at the level of the monomeric units is still not completely elucidated.

The first proposal for the structure of the stereocomplex of it- and st-PMMA was given by Liquori et al.³ On the basis of the analogy between fiber diagrams of crystalline it-PMMA and the stereocomplex, they concluded that the conformation of the isotactic chain in the complex was the same as that in crystalline it-PMMA, at that time assumed to be a 5/1 helix.⁴ They proposed a model for the stereocomplex in which flat syndiotactic chains lie in the grooves of the 5/1 isotactic helices, tilted by about 60° with respect to the helix axis. Although this model could not explain the phenomenon of template polymerization,^{5,6} it lasted about 20 years before another model was proposed.

After a long period of controversy, Tadokoro et al. showed that crystalline it-PMMA consisted of a 10/1 double-stranded helix, in which the conformation of both isotactic chains is close to the extended-chain form (trans-trans in the staggered approximation).^{7,8} They also suggested that the structure of the stereocomplex was closely related to this double helix. Špeváček and Schneider reported that their results of an NMR study were compatible with this idea.⁹ In addition, for a double-stranded helical structure, template polymerization should be possible. At the same time, it became possible to obtain stretched fibers of solvent-stabilized crystalline st-PMMA, and Tadokoro et al. showed that crystalline st-PMMA has a 37/4 helical structure with a large radius, with a pitch of 8.9 Å, while solvent molecules are included in the cavity within the helix.^{10,11} Also in this structure, the chains have an extended trans-trans conformation.

On the basis of the strong analogy between the fiber diagrams of the stereocomplex and solvent-stabilized crystalline st-PMMA, Bosscher et al. investigated whether it-PMMA plays the same role as the solvent in crystalline st-PMMA. They found that stereocomplexation was also possible when the methyl group of the ester of st-PMMA was replaced by an *i*-butyl group, while a modification of the ester group of it-PMMA prevented complexation.¹² On the basis of these observations, the established 1/2 isotactic/syndiotactic unit stoichiometry,¹³ fiber X-ray data,

and conformational energy analyses,¹⁴ they suggested for the structure of the complex a 30/4 double-stranded helix, in which the asymmetric unit consists of 1 isotactic unit and 2 syndiotactic units. However, the fiber diagrams showed only 10 independent reflections, which were rather broad, and also no meridional reflection was observed; so it was not possible to verify the proposed symmetry.

From various experimental investigations, employing different techniques,¹⁵⁻²⁵ and from conformational energy analyses,²⁶⁻²⁹ it is known that the trans-trans conformation is energetically the most favorable for it-PMMA as well as st-PMMA. From infrared spectroscopy investigations, it appeared that st-PMMA^{22,23} as well as it-PMMA^{17,25} in the stereocomplex also have a backbone conformation close to all-trans, a finding that does not support the model of Bosscher et al., in which only the isotactic chain has a conformation close to all-trans.

As until now, it is not possible to explain the formation of the stereocomplex in terms of an interaction between specific sites on the complementary chains; it is suggested that the driving force for complexation might be a good sterical fit between the two chains, stabilizing each other's energetically most favorable (close to all-trans) conformation, by van der Waals forces. This hypothesis was the starting point for a new X-ray fiber diffraction study on the structure of the stereocomplex.

Experimental Section

The samples were analyzed with a Statton photographic X-ray camera using Ni-filtered Cu K α radiation. The stretched fibers of stereocomplex from it-1 and st-1 are the same as used in ref 13 and 20.

It-2 ($M_w = 2.4 \times 10^5$; $D = 1.15$; isotactic triads >95%) is a fraction of the product of a polymerization in toluene using phenyl magnesiumbromide as initiator. St-2 ($M_w = 2.4 \times 10^5$; $D = 1.25$; triad tacticity, $i/h/s = 5/30/65\%$) is a fraction of the product of an ordinary radical polymerization. For synthesis and characterization procedures, see ref 30.

Fibers of it-2 and st-2 were obtained by mixing 3 wt % acetone solutions in a 1/1 ratio. A total of 2 h after mixing, the gel obtained was stretched manually.

Results and Discussion

Fiber Diffraction. Various fiber diagrams were made for different tilt angles, employing a range of exposure times. The most important result was that, employing a tilt angle of about 23°, a weak and broad meridional reflection was observed at the ninth layer line. Apart from this, also some other very weak and broad reflections not

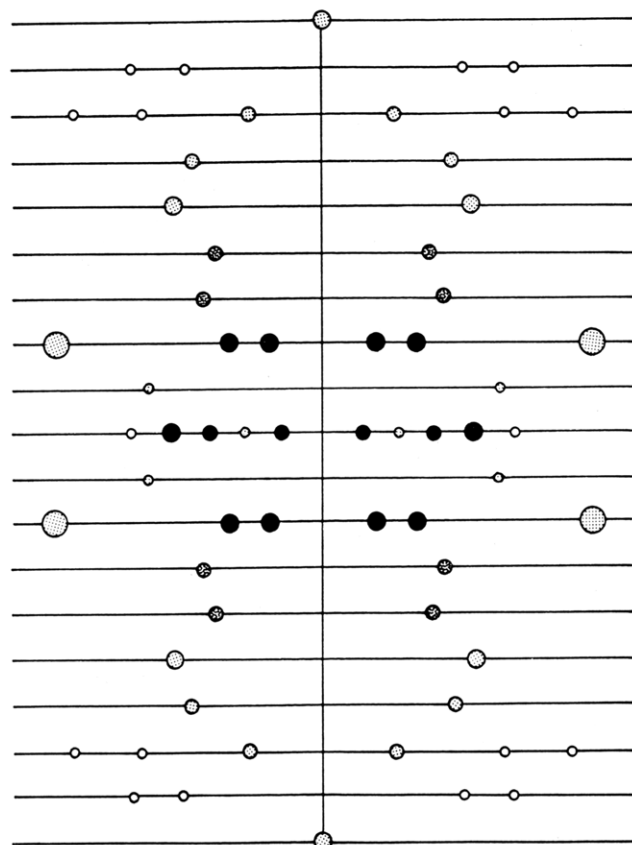


Figure 1. Schematic representation of the observed reflections of the stereocomplex from it-1 and st-1, as composed from various fiber diagrams. Although all reflections, especially on the higher layer lines, were observed as arcs, they are presented here as circles. The relative intensities are given in a qualitative sense, varying from strong (●) to very weak (○). The width of the reflections are indicated qualitatively by the radii of the circles.

reported before were observed, the most important of which is the one observed on the first layer line, as in previous studies, this layer line was reported to be absent.^{3,14} In Figure 1 the results are summarized.

Since only broad reflections are observed, it is suggested that the diffraction pattern is for the major part determined by the structure of the helices; i.e., the additional ordering of the helices is low, which enables us to describe the diffraction pattern in the first instance in terms of helical diffraction.

According to Crick et al., the scattered amplitude on a layer line l of a helical structure is given by^{32,33}

$$F(R, \psi, l/c) = \sum_n G_{n,l}(R) \exp(in(\psi + \pi/2)) \quad (1)$$

$$G_{n,l}(R) = \sum_j f_j J_n(2\pi R r_j) \exp[i(-n\phi_j + 2\pi l z_j/c)] \quad (2)$$

Here R and ψ are cylindrical coordinates in reciprocal space. r_j , ϕ_j , and z_j are the cylindrical coordinates in real space of the atoms belonging to the asymmetric unit. c is the fiber identity period, and n is the order of the Bessel function $J_n(2\pi R r_j)$ contributing to layer line l .

This expression is essentially the Fourier transform of a structure periodic in z . The helical symmetry is accounted for by a selection rule stating that only the orders n of the Bessels contribute to a layerline l , for which the following expression holds:

$$l = tn + um \quad (3)$$

Here u is the number of asymmetric units per t turns of the basic helix, while m and n are integers.

Table I
Geometrical Parameters Employed To Construct the 9/1 Double-Stranded Helix

bond length, Å	bond angle, deg	torsion angle, deg
$\alpha\text{C}-\text{CH}_2$, 1.53	$\text{C}-\alpha\text{C}-\text{C}$, 106	$\theta(\text{it})$, 4
$\alpha\text{C}-\alpha\text{CH}_3$, 1.53	$\alpha\text{C}-\text{C}-\alpha\text{C}$, 124	$\theta'(\text{it})$, 33
$\alpha\text{C}-\text{C}^+$, 1.52	$\text{C}-\alpha\text{C}-\text{C}^+$, 111	$\theta(\text{st})$, 3
$\text{C}^+=\text{O}$, 1.22	$\alpha\text{C}-\text{C}^+=\text{O}$, 122	$\theta'(\text{st})$, -6
C^+-O , 1.36	$\alpha\text{C}-\text{C}^+-\text{O}$, 114	$\chi(\text{it})$, 180
$\text{O}-\text{C}'$, 1.45	$\text{O}-\text{C}^+=\text{O}$, 124	$\chi_i(\text{st})$, 180
	$\text{C}^+-\text{O}-\text{C}'$, 110	$\chi_{i+1}(\text{st})$, 0

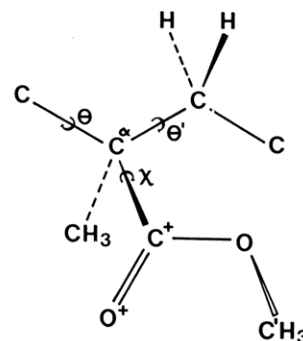


Figure 2. Schematic representation of a structural unit of PMMA, showing the various geometrical parameters employed.

Model. Bosscher et al. already calculated from the observed layer-line spacing a fiber identity period of $c = 18.4 \text{ Å}$,¹⁴ which is consistent with our data. The meridional reflection on the ninth layer line is consistent with a 9/1 helix. It is not possible to decide from the present data whether it is a real commensurable helix. Next, 9/1 double-stranded helices were constructed with an asymmetric unit of 1/2 isotactic/syndiotactic units having a pitch of 18.4 Å . The geometrical parameters used, assuming a close to all-trans conformation of both chains, were adopted from the work of Vacatello et al.²⁹ and are given in Table I. The 9/1 helical symmetry was accounted for by adaptation of the torsional angles θ and θ' (see Figure 2). For the ester torsion angles χ , measured relative to the α -methyl group, only values of 0 (cis or syn) or π (trans or anti) were considered.

Since the quality of the diffraction patterns is still rather poor, making a quantitative analysis impossible, an extensive optimization procedure was considered not to be useful. Therefore, only the relative rotation of the two intertwined chains with respect to each other and the ester rotation angles χ for both polymers were varied (0 or π). Of each structure the potentially averaged molecular structure factor for each layer line was calculated. The values of the atomic scattering factors were taken from ref 34. For the isotropic temperature factor, a value of 8 Å^2 was adopted. The scattering of the hydrogen atoms was not taken into account. The results for the best fit obtained, employing the geometrical parameters of Table I, are presented in Figure 4; the corresponding structure is given in Figure 3. In this structure the syndiotactic chain is rotated -80° with respect to the isotactic chain.

The observed reflections on the equator can only partly be explained in terms of helical diffraction, and they are ascribed to the packing of the helices. No better results were obtained than already published by Vorenkamp et al.¹³ The results obtained for the molecular structure factor, compared to the observed reflections, in particular the strong but broad reflections at $R = 0.048 \text{ Å}^{-1}$ and $R = 0.179 \text{ Å}^{-1}$, suggest a tentative monoclinic unit cell with $a' = 21.5 \text{ Å}$, $b' = 16.5 \text{ Å}$, and $\gamma' = 112^\circ$, which is not excluded by packing considerations. However, still not

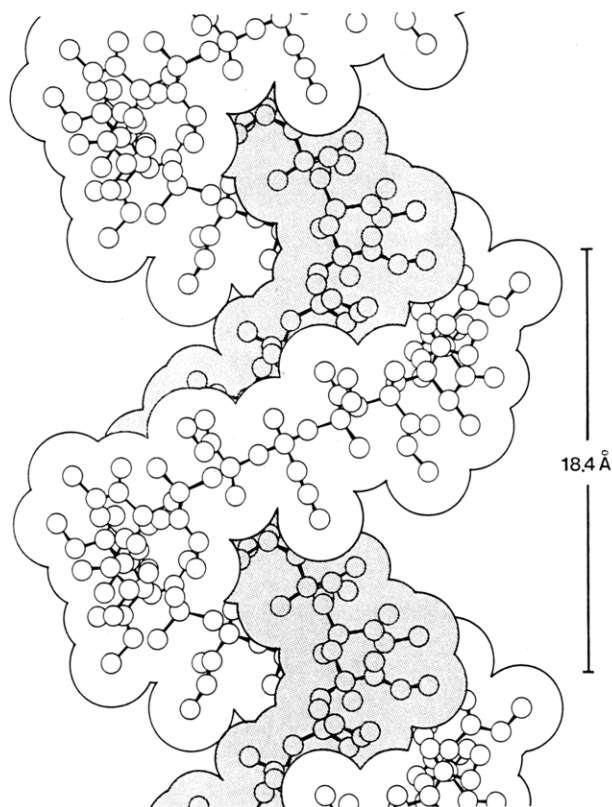


Figure 3. Molecular model of the proposed 9/1 double-stranded helix of the stereocomplex of it- and st-PMMA. The isotactic chain (shaded) is surrounded by the syndiotactic chain.

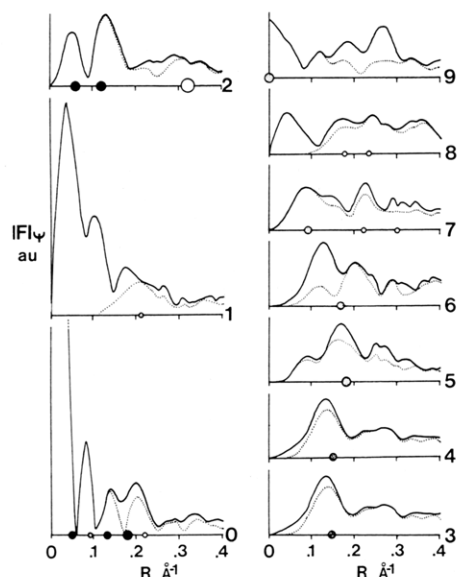


Figure 4. Rotationally averaged absolute values of the molecular structure factors $|F|_\psi$ for the layer lines $l = 0-9$, as calculated from eq 1 with (—) and without (···) the odd Bessel contributions of lowest order, as given by eq 3. The observed reflections are indicated in the figure, using the same symbols as in Figure 1.

enough data are available to make some definite conclusions on the unit cell and space group.

With respect to the higher layer lines, it appears that, only for the layer lines without a contribution of odd Bessels of low order, a qualitatively reasonable fit is obtained. If the odd Bessels of lowest order contributing to a layer line are omitted, a better fit is obtained (dotted lines in Figure 4), which is especially apparent for layer lines 1 and 8, to which in principle Bessels of order 1 and -1, respectively, do contribute, which are not observed. A



Figure 5. Schematic representation of the proposed disorder in the structure of the stereocomplex. The dotted lines represent the correlation with a four-stranded helix, having a 2-fold rotation axis of symmetry.

possible explanation could be that we deal with a true double helix showing 2-fold rotational symmetry, in which case odd-ordered Bessels are not observed,³³ but this would mean that we deal in fact with a four-stranded helix. Chain-packing considerations do not exclude this possibility. However, from a kinetic point of view, knowing that in the bulk complexation proceeds within the time scale of minutes, almost independent of chain length,³⁵ this suggestion is not realistic. Considering also that we do not deal with perfectly tactic polymers, it is highly improbable that four-stranded structures are formed of reasonable length.

During the molecular modeling procedure, it appeared that there are in principle two possibilities for a good sterical fit between the two intertwined chains, one of which is shown in Figure 3, the other one is obtained by shifting the two chains with respect to each other for about half the pitch (or by rotating the chains for about π with respect to each other). From the present data, it is not possible to make a distinction between them. One can imagine that, in case of an error in one of the chains (tacticity, chain ends, loops), the other chain preserves its helical conformation but that the rotational orientation of the first one with respect to the other chain is changed by an angular factor of about π . A schematic representation of the proposed regular disorder in the structure is given in Figure 5.

Influence of Disorder. We investigated whether it is possible that the absence of odd Bessels of low order is caused by the kind of errors in the proposed structure, depicted above. As a model we consider a structure, periodic in z with a new identity period c^+ , consisting of τ "trains" of residues with length N_1, N_2, \dots, N_τ . Each train has a 9/1 helical symmetry but is rotated with an angle π with respect to the previous train. Expressing c^+ in terms of c , by means of a constant of proportionality K_c , $c^+ = K_c c$, and furthermore also expressing the z coordinate of residue j of train k in terms of c ($z_{1,1} = 0$):

$$Z_{k,j} = (j + \sum_{h=1}^k N_{h-1})c/9 \quad (4)$$

We obtain from eq 2, assuming that $r_{k,j} = r$, $f_{k,j} = f$, and $\phi_{1,1} = 0$:

$$G_{n,l^+}(R) = \sum_{k=1}^{\tau} \sum_{j=1}^{N_k} f J_n(2\pi R r) \exp(i\alpha_{k,j}) \quad (5)$$

$$\alpha_{k,j} = (2\pi/9)(l^+/K_c - n)(j + \sum_{h=1}^k N_{h-1}) - n\pi(k-1) \quad (6)$$

In this expression l^+ represents the layer-line number that belongs to the identity period c^+ . From the definition of c^+ , it follows that $l = l^+/K_c$. Although eq 5 is not easy to handle whenever the sequence length distribution is not known, it is not difficult to see that the contribution of the even Bessels to a layer line l ($l^+/K_c = \text{integer}$) is identical with the case of an infinite perfect 9/1 helix. This does not hold for the odd Bessel contributions. The first part

of the expression for α_{kj} represents the contribution of the periodicity in z . The second part takes into account which of the two possible angles, ϕ_j or $\phi_j + \pi$, is the position of residue j . If the nine possible angles $\phi_j = j2\pi/9$ are equally populated by ϕ_j or $\phi_j + \pi$, all over c^+ , then $G_{n,l^+}(R) = 0$, for $n = \text{odd}$, and for all values of l^+ . This condition is approached for $c^+ \rightarrow \infty$, provided, of course, that the sequence length distributions for $k = \text{odd}$ and $k = \text{even}$ are equal. This brings us to the additional layer lines l^+ ($l^+/K_c \neq \text{integer}$), arising from the assumed periodicity c^+ . From the general theory of diffraction we know that, for $c^+ \rightarrow \infty$ or whenever there is no additional periodicity c^+ , in principle, a continuous distribution of intensities, instead of distinct layer lines, is found. However, for our case the periodicity arising from the helical trains remains, and therefore only those layer lines, for which $l^+/K_c = \text{integer} = l$, give still an essential contribution to the diffraction pattern, and for these layer lines, apart from the normal helical selection rule, the additional condition $n = \text{even}$ holds, provided that there is a real random distribution of train sequence lengths.

This result is easily extended to the case of a double-stranded helix, having two residues at r and r' as an asymmetric unit. If the sequence length distributions of the trains, in between the rotational jumps of π in both helices are really random, the contributions of odd Bessels arising from both kinds of residues for the trains $k = \text{odd}$ interfere destructively with their $k = \text{even}$ counterparts.

We have now shown that a random distribution of helical train sequences, related to each other by an angular discontinuity of π , may give rise to a helical diffraction pattern characteristic for a structure with a 2-fold rotational symmetry. It is expected that the condition of a random distribution is in practice met when the overall structure is long enough to make destructive interference of (or most of) the odd-ordered Bessel contributions possible. In this respect, it is interesting to note that Bosscher et al. found that, for the case of the stereocomplex of it-PMMA and st-poly(methacrylic acid), qualitatively the same diffraction pattern is obtained.¹⁴ However, for this case the reflections, now recognized as the odd-ordered Bessel contributions, were observed, but they were still weak. It is also known that those complexes are less easily obtained, and the diffraction patterns show only some reflections on layer lines of low order for low values of R ,¹⁴ suggesting a less ordered structure compared to the it-PMMA/st-PMMA stereocomplex. For such a case destructive interference between the helical trains is expected to be less complete. Another explanation could be that because of the absence of the ester groups of the syndiotactic chain, the two possibilities of intertwining the chains are not related to each other by a rotation close to π , but $\Delta\phi$, in which case the degree of destructive interference between odd-ordered Bessels is dependent on the order of the Bessel contribution n , because now the second part of eq 6 is replaced by $n\Delta\phi(K-1)$. This might also explain the fact, suggested from the diffraction pattern of the it-PMMA/st-PMMA stereocomplex, that higher values of $n = \text{odd}$ do contribute to the layer lines; viz. $\Delta\phi$ is close to, but not exactly, π .

Comparison with Previous Results. Apart from the present X-ray data, also several experimental observations published before are in favor of the proposed model.

It was already indicated in the introduction that the close to all-trans conformation is energetically the most favorable for both polymers,¹⁵⁻²⁹ and it was shown from IR investigations that also in the stereocomplex both polymers have this conformation.^{17,22,23,25} We have shown

that a close to all-trans conformation is compatible with the observed 9/1 helical symmetry. Moreover, the proposed conformations are very close to the conformations of the polymers in their crystalline state: a 10/1 helix for it-PMMA^{7,8} and a 37/4 helix for the solvent-stabilized crystal of st-PMMA.^{10,11}

Bosscher et al. showed that, in case of a modification of the st-ester group, even when the methyl group is replaced by an *i*-butyl group, stereocomplexes are still formed, while each modification of the it-ester group prevents complexation.¹² The present model of the double-stranded helix has rather large grooves, and, moreover, the ester groups of st-PMMA are all pointing outward, making a modification possible, in line with the observations of Bosscher et al. The it-PMMA ester groups are all pointing towards the syndiotactic backbone, which is compatible with the observation that even an ethyl ester instead of a methyl ester prevents complexation.¹²

In the present model, apart from the st-ester groups, also the st- α -methyl groups are pointing outward; therefore, an error with respect to the tacticity of the syndiotactic chain destroys not necessarily the structure. Moreover, as a consequence of the large grooves in both helical chains, there are two possibilities of intertwining the chains and, consequently, larger errors in tacticity can be dealt with efficiently. These properties of the proposed structure may explain the fact that even st-PMMA of very low tacticity ($i/h/s \approx 5/50/45\%$) is still able to form complexes with it-PMMA.³⁶

It is interesting to note that it appears from molecular models of the proposed structure, that, whenever the configuration of it-PMMA changes from ...ddd to ll..., only a torsional rotation of two backbone bonds at the location of the error is enough to preserve the overall helical complex structure, introducing only a rotational jump in the isotactic helix, without a change of the conformation of the syndiotactic chain.

The fact that the diffraction pattern clearly shows helical symmetry, while the two polymers are not perfectly tactic, is also an indication for the tolerance of the overall helical structure of the complex with respect to errors. Using first-order Markov statistics,³⁷ it is possible to estimate the configurational sequence distribution of both polymers. It appears that, for tacticities of about 90%, 2/3 of the sequences are shorter than 40 units. Considering also the errors originating from chain ends, loops, and bridges between two complexed sections, it is expected that truly perfect complexed sections are for the major part not much longer than the pitch of the proposed structure. Nevertheless, still a helical diffraction pattern is observed, which can be explained in terms of the proposed two-state rotational disorder, as in that case the overall helical symmetry is preserved.

In addition, complexed material, obtained after mixing 3 wt % acetone solutions of isotactic and atactic PMMA ($i/h/s = 5/30/65\%$), was stretched. The resulting fiber diagram is given in Figure 6, and we see that the main characteristics are still present, although for the atactic sample, according to first-order Markov statistics,³⁷ 2/3 of the syndiotactic sequences are even shorter than 10 units. This result again subscribes the tolerance of the overall structure with respect to errors.

Concluding Remarks

We have shown that the fiber diffraction pattern of the stereocomplex can be explained in terms of a two-state rotationally disordered 9/1 double-stranded helix, having an asymmetric unit consisting of 1 isotactic unit and 2 syndiotactic units. From the proposed structure, it is

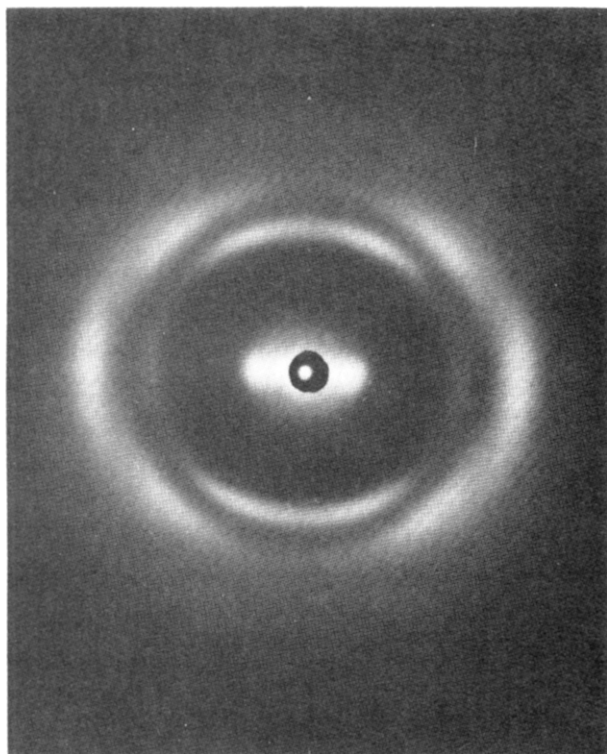


Figure 6. Fiber diffraction pattern shown by stretched complexed material obtained 2 h after mixing 3 wt % acetone solutions of it-2 and st-2 (1/1 w/w).

suggested that the driving force for complexation is a good sterical fit between the two chains, stabilizing each other's energetically most favorable conformation by van der Waals forces.

As the diffraction data are still poor, the proposed model is not optimized, and it should be considered as a starting point for further investigations.

In principle, an extensive conformational and packing analysis can present additional information on the structure. However, the geometrical parameters of the most favorable conformation of both polymers, as they were found by Vacatello et al.,²⁹ are very close to the parameters employed to describe the structure; therefore, it is expected that such an analysis would only give additional information on the possibilities of intertwining the chains. The present results suggest that the overall structure, and in particular the packing of the chains with respect to each other, is for an important part determined by the tendency of the system to deal as efficiently as possible with the structural errors, and so only an extensive analysis taking these errors into account will be useful.

Registry No. Isotactic PMMA-syndiotactic PMMA complex, 120085-49-6.

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