

Coiled-coil molecular model for isotactic polystyrene gels

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To explain the characteristics of X-ray scattering by isotactic polystyrene dry gels, a coiled-coil molecular model is proposed instead of the previously reported almost fully extended 12/1 helix having sixfold helical symmetry (per dimer). The coiled-coil chain is assumed to have basically the same 3/1 helical structure of $(-TG-)_3$ conformation as in the crystalline phase and the 3/1 helix axis itself again makes a large helix having a long pitch. The observed chain repeat length of 30.6 Å comprises six turns of the 3/1 helix (a total of 18 monomer units) in one turn of the large helix: the 3/1 helix axis itself makes a large helix of 4.08 Å radius and tilts by about 40° from the direction of stretch. The coiled-coil can be expressed again in terms of a single 6/1 large helix in which the asymmetric unit comprises three monomer units in one turn of the original 3/1 helix. Since the 3/1 helix axis tilts by about 40°, the axial length of the asymmetric unit becomes 5.1 Å ($6.65 \text{ Å} \times \cos 40^\circ$): the strong 5.1 Å meridional reflection comes from the asymmetric unit. Although the detailed structure cannot be defined at this stage, because of uncertainty about the unit cell and the solvent content which contributes coherently with the polymer to the X-ray scattering, the molecular transforms of several coiled-coil models possessing different helical senses seem to explain the characteristics of the X-ray scattering.

(Keywords: isotactic polystyrene gel; gel structure; coiled-coil chain model; X-ray diffraction; molecular transform)

INTRODUCTION

Since Keller and coworkers¹ commenced an X-ray study on isotactic polystyrene (iPS) gels² in 1976, many structural studies on wet and dry iPS gels at the molecular or morphological level have been reported^{3–14}. Although there is a confusing variety of experimental data and results, we have to accept the X-ray evidence for the stretched dry gels that the chain repeat length is ~ 30.6 Å and the most intense 5.1 Å meridional reflection on the 6th layer line might be indicative of an inherent structural unit of the gels irrespective of the kind of solvent used. However, except for the earliest assumption that the 5.1 Å reflection comes from head-to-head or syndiotactic sequences, the almost fully extended 12/1 helix of sixfold helix symmetry (per dimer)^{4,5} is still under discussion. In fact, it seems that this helix model, even if some modifications by internal rotations are feasible, hardly explains the characteristics of the X-ray diffraction patterns. Recent studies^{8,10,14} support the nearly 3/1 helical structure as in the crystalline phase rather than the extended 12/1 helix. However, no detailed structure that can explain the features of the X-ray scattering has been proposed.

If we are certain about the assumption that the chain repeat length of 30.6 Å comprises 12 monomer units, we have to accept an almost fully extended conformation, such as the 12/1 helix (because the average axial length

per monomer unit is $30.6/12 = 2.55$ Å). However, as far as we are aware, there is no assertive evidence that the observed chain repeat length of 30.6 Å comprises 12 monomer units. Alternatively, assuming that the 3/1 helix of $(-TG-)_3$ conformation¹⁵ in the crystalline phase is basically retained in the gels, we obtain a quite different model, that is, a coiled-coil where the 3/1 helix axis itself again makes a large helix (probably due to solvation). As shown later, the basic structure of the coiled-coil proposed in this paper is such that the observed chain repeat length of 30.6 Å comprises six turns of the 3/1 helix (small helix) in one turn of the large helix. Accordingly, the number of monomer units in the chain repeat is 18 instead of 12.

COILED-COIL MODEL

First the basic idea of the coiled-coil model will be presented. The coiled-coil model is shown schematically on the left-hand side of *Figure 1*, in which the continuous small helix represents the 3/1 helix of $(-TG-)_3$ conformation, the radius of which is expressed by that of the main chain carbon atoms, and the phenyl groups are omitted for simplicity. The development surface of the coiled-coil obtained by cutting *Figure 1* (left) along the chain direction (the large helix axis parallel to the direction of stretch) is shown in *Figure 1* (right). The vertical axis is parallel to the chain direction, and the height of the rectangle is the observed chain repeat length, 30.6 Å. Assuming that six turns of the 3/1 helix (having a chain repeat length of 6.65 Å as in the crystalline phase)

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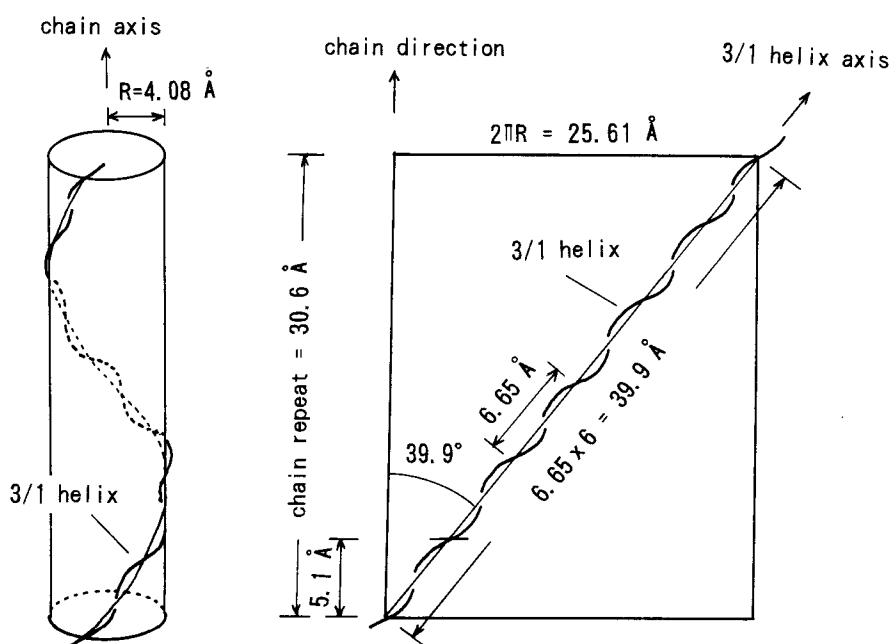


Figure 1 Coiled-coil chain model (left) and its development surface (right)

are contained in one turn of the large helix which makes the complete chain repeat of 30.6 Å, the 3/1 helix axis will tilt by 39.9° from the chain direction. Again from the width of the rectangle in Figure 1 (right), which corresponds to the circumference made by the large helix that is the trace of the small helix axis, the radius of the large helix is calculated to be 4.08 Å. It is noted that the projection of the chain repeat of the 3/1 helix onto the chain axis becomes 5.1 Å, the most important quantity which has been always the focus of discussion. That is, the structural unit giving the 5.1 Å meridional reflection is represented by one turn of the original 3/1 helix: three monomer units in one turn of the original 3/1 helix are, if the coiled-coil is uniform, equivalent to one another along the coiled 3/1 helix axis but no longer equivalent with respect to the chain direction, because of the tilting of the 3/1 helix axis. Then when the three monomer units in one turn of the original 3/1 helix are adopted as the asymmetric unit, the coiled-coil can be regarded as a simple 6/1 (large) helix. In either expression, systematic appearance of meridional reflections can be expected on the 6th (5.1 Å), 12th, 18th layer lines and so on.

EXPERIMENTAL

iPS with a weight-average molecular weight of 1.55×10^6 ($M_w/M_n = 4.46$) and a diad isotacticity greater than 99% was kindly supplied by Idemitsu Kosan Co., Ltd. For the present purpose, we tried to prepare uniaxially oriented iPS dry gels giving as many gel X-ray reflections as possible. In other words, the contribution of free solvent to the X-ray scattering (which gives broad halos) was minimized by removing free solvent. *Cis*- and *trans*-decalins and hexahydroindan were used as solvents. Among them, *cis*-decalin was exclusively used in this study. About 15–20 wt% *cis*-decalin solutions of iPS were quenched in ice water, stretched about three to four times the original length and then dried at room temperature for several hours. These samples were subjected simultaneously to X-ray and thermogravimetric measurements. Figures 2a and b are the X-ray gel patterns

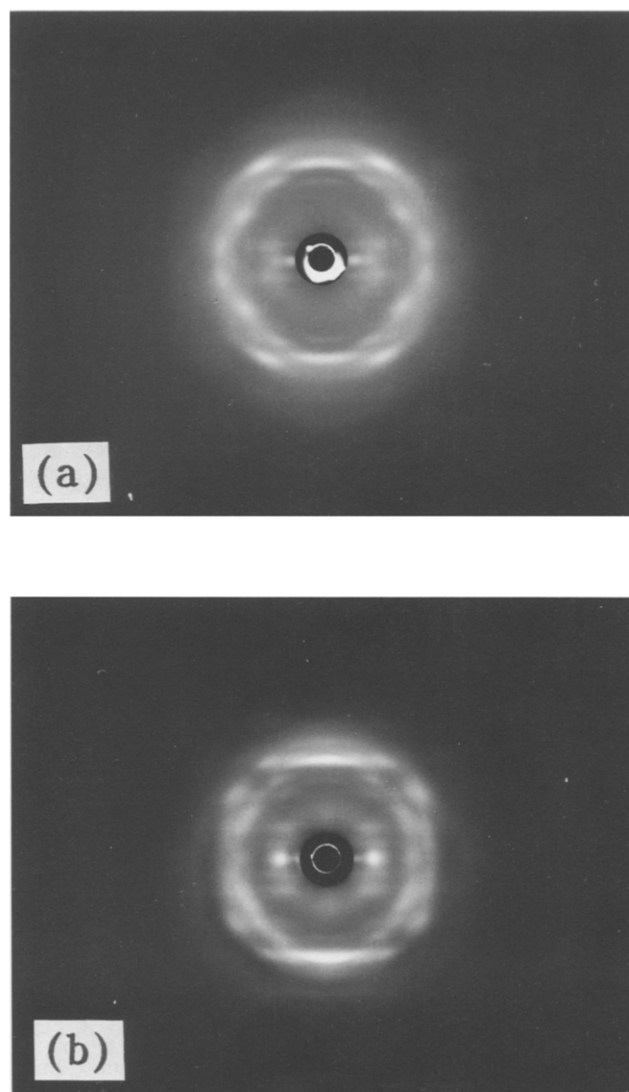


Figure 2 X-ray diffraction patterns for iPS dry gels having molar ratio (monomer:*cis*-decalin) of (a) 4.8:1 and (b) 6.7:1

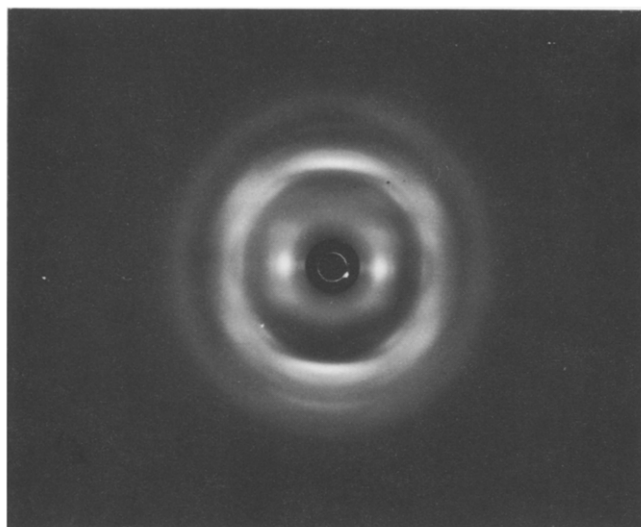


Figure 3 X-ray diffraction pattern for an iPS/hexahydroindan dry gel

thus obtained, and the molar ratios of monomer:decalin for the two samples (samples a and b) estimated from the thermogravimetric measurements were 4.8:1 and 6.7:1, respectively. *Figure 3* is an X-ray pattern for an iPS/hexahydroindan dry gel. Polarized i.r. absorption measurements were also performed for a stretched iPS/*cis*-decalin dry gel, which was confirmed by X-ray analysis to correspond to sample a, and its annealed sample which was transformed to the 3/1 crystalline phase.

RESULTS AND DISCUSSION

The X-ray patterns so far reported together with ours for many kinds of sample of both wet and dry iPS gels change in the relative intensities of reflection depending on the type and content of the solvent. In practice, *Figures 2a* and *b* are different in intensity distribution: sample b exhibits the 2nd layer line with moderate reflection intensities, while sample a does not, and the positions of reflections are evidently different even on the equator. This indicates that the states of aggregation of the polymer chains involving rotational disorder and conformational disorder and/or the behaviour of the solvent molecules in the two samples are appreciably different. However, the chain repeat length is almost the same and there exists the strong 5.1 Å meridional reflection for both iPS/*cis*-decalin gels and also iPS/hexahydroindan gel (*Figure 3*). It is therefore certain that both polymer chains and solvent molecules contribute coherently to the X-ray scattering. Besides *Figures 2a* and *b*, we obtained an X-ray photograph for sample a by tilting the sample to the incident X-ray beam to measure higher layer lines: we could see meridional reflections on the 6th (strong), 12th (weak) and 18th (very weak) layer lines. Again many higher layer lines, 7, 8, 9, 10 and 15th layer lines, could be observed.

To make the coiled-coil model a more detailed one, it is needed to assert the helical sense for both large and small helices, i.e. right- or left-handed, and also the rotational position of the asymmetric unit about the small helix axis involving freedom in internal rotation of the phenyl groups in the asymmetric unit. Numerous models are thus generated. At the present stage, the unit cell cannot be defined because of the poor crystallinity, and

the solvent content which contributes coherently to the X-ray scattering with the polymer chains is also uncertain. Therefore no detailed structure can be defined. However, several coiled-coil models examined gave strong intensities for 6, 12 and 18th meridional reflections. In addition, most layer lines gave moderate intensities near the meridian as observed. One example of a coiled-coil model and its molecular transform are shown in *Figures 4* and *5*, respectively. Of course the contribution of solvent is not included in the calculation. As already mentioned, the X-ray patterns for the two samples with different solvent contents are different from each other, indicating that the contribution of solvent to the X-ray

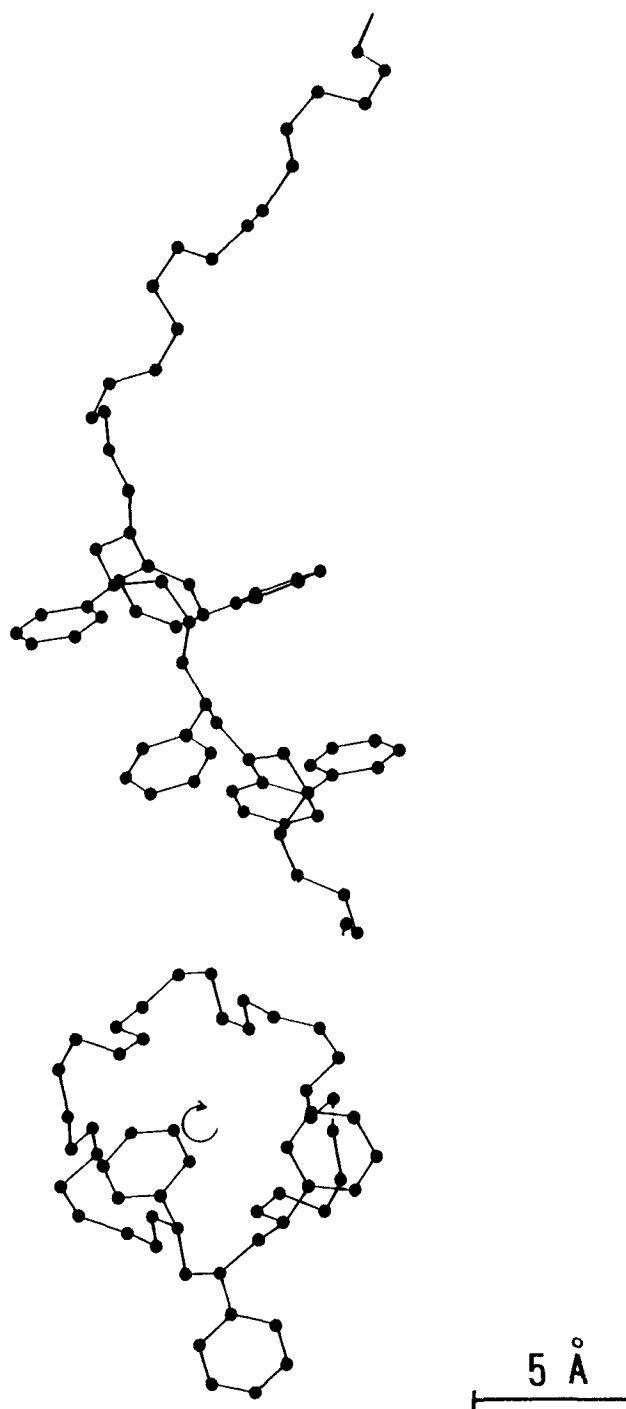


Figure 4 Example of coiled-coil iPS chain. Both large and small helices are left-handed. Only a few phenyl groups are drawn for simplicity

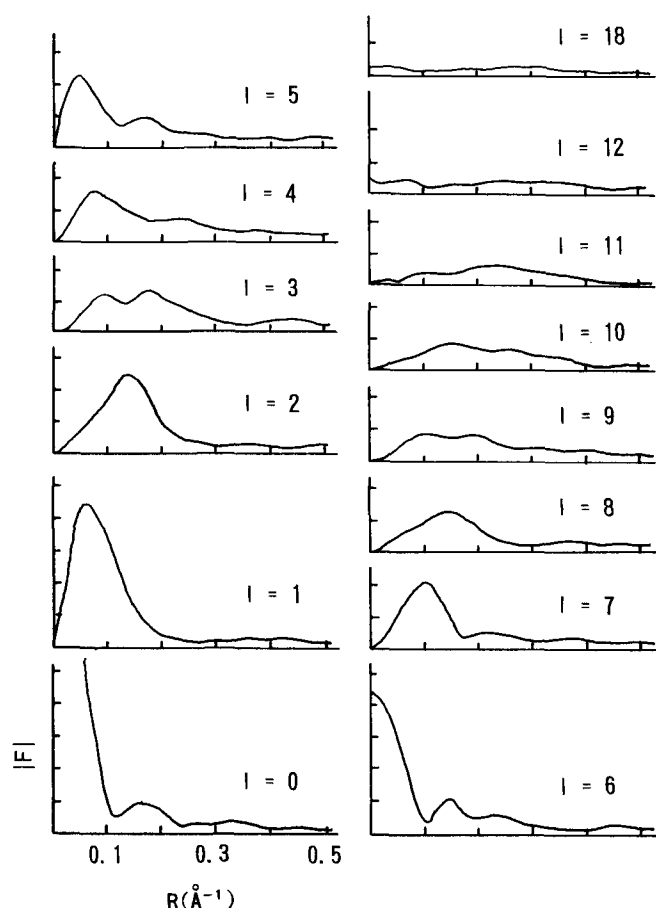


Figure 5 Molecular transform for the model shown in Figure 4

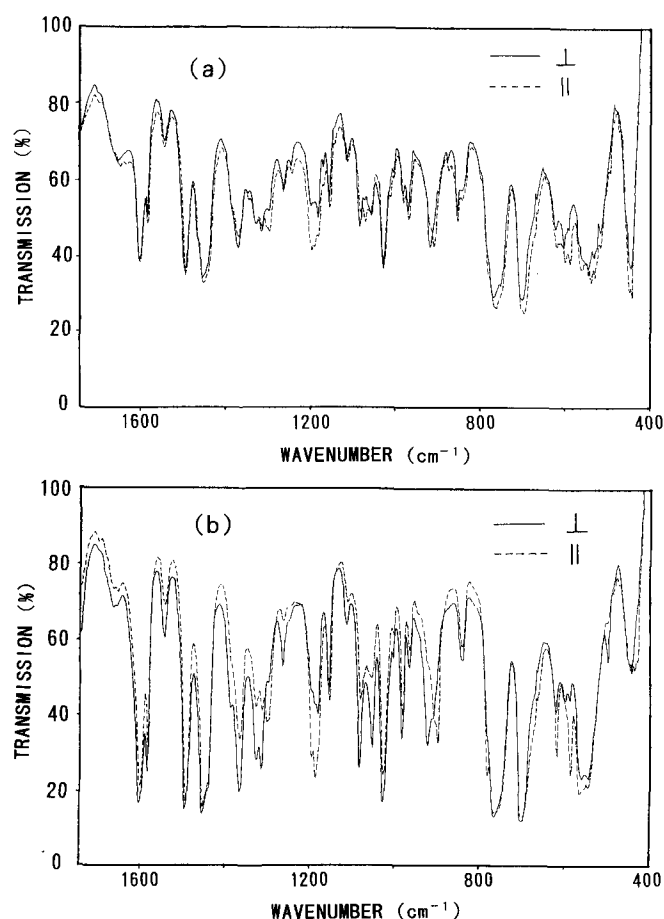


Figure 6 Polarized i.r. spectra for (a) a dry gel (*cis*-decalin) and (b) 3/1 helix crystal obtained by annealing of sample a

scattering cannot be ignored. In addition, the three monomer units in the asymmetric unit of the 6/1 large helix are no longer equivalent to one another as already noted. This feature does not require that the coiled-coil must be uniformly coiled. Then, although the molecular transforms for the polymer chain alone do not always interpret well the observed X-ray patterns, the characteristics of the patterns seem to be explained by such coiled-coil models.

Kobayashi and coworkers^{11,13,14} pointed out that the i.r. absorption bands for an iPS/CS₂ gel rather resemble those of the crystalline sample (3/1 helix), and the slight difference between the two is attributed to differences in intra- and interchain interactions between the two phases. Polarized i.r. spectra shown in Figures 6a and b for sample a and subsequently annealed sample a, which was fully transformed to the 3/1 crystalline phase, respectively, gave almost the same results in the 1400–800 cm⁻¹ range as previously reported^{6,7,14}, except for a few weak bands from *cis*-decalin in sample a. It is noticeable that the previous results obtained for wet gels (after subtracting the bands from the solvent) are essentially identical to the spectrum of the present dry gel. Although no characterization by X-rays was given for the wet gels, it is likely that the polymer chains take basically similar conformations in both wet and dry gels, even if the degrees of structural order in both states differ to some extent. Next consider the dichroism of the bands for the dry gel and the resulting 3/1 helix crystal. Based on the coiled-coil model, the coiled 3/1 helix axis tilts by 40° from the direction of stretch. The phase change from the gel state to the crystalline state on annealing involves straightening of the coiled 3/1 helix axis and alignment of the 3/1 helix axis to the direction of stretch. This feature was confirmed by X-rays: the annealed sample exhibited the well uniaxially-oriented fibre pattern of the 3/1 helix crystal. As shown in Figures 6a and b, the dichroic ratios of most bands of the crystalline sample are greater than those of the gel. This feature is again explained in terms of the change of the orientation of the polymer chain axis on the phase transition.

In any case, a coiled-coil model that basically explains the principal features of the X-ray diffraction of iPS dry gels seems worthy of being further examined from some aspects.

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