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Crystal Structure of Poly(*p*-phenylene sulfide): A Refinement by X-ray Measurements and Molecular Mechanics Calculations

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ABSTRACT: Samples of poly(*p*-phenylene sulfide) obtained by different thermal and/or mechanical treatments are found to exhibit the same crystal structure. Conformational and packing analysis performed by molecular mechanics have given the lowest energy conformation of the polymer chain in the crystal state and the lowest energy crystal structure. The intensities of the observed reflections measured by a powder diffraction profile have been compared with the calculated intensities for different models of chain conformations and crystal structures. The lowest discrepancy index between calculated and observed intensities is obtained for a structure in very good agreement with that postulated by molecular mechanics.

Introduction

Poly(*p*-phenylene sulfide) (PPS) is a polymer having scientific and industrial interest due to its high-temperature and high-strength properties and to its electrical properties upon doping with strong electron acceptors.[1−6] The crystal structure of PPS was reported by Tabor et al.,[7] who performed X-ray studies on oriented films. The proposed unit cell was orthorhombic with $a = 8.67$ Å, $b = 5.61$ Å, and $c = 10.26$ Å, space group *Pbcn*. The sulfur atoms of the molecular chains were positioned in a *zigzag* manner in the (100) planes, and the phenylene groups were placed alternately at +45° and −45° with respect to the same planes, that is, in a symmetric way. A comparison between the calculated and the observed intensities was carried out in a semiquantitative way. Subsequently, Garbarczyk[8] suggested a different structure for PPS on the basis of structural data for small molecular model compounds along with simple intra- and intermolecular energy calculations. In particular, Garbarczyk assumed that the C−S−C angles were within the range 103°−107° and proposed an asymmetric structure where pairs of phenylene rings, one nearly coplanar with the C−S−C plane and the other inclined from this plane at about 60°, succeeded alternately. Moreover, using independent X-ray data for PPS powders, Garbarczyk obtained interplanar distances and intensity reflections different from those reported by Tabor et al. Later, Lovinger et al.,[9] by electron microscopy study of single crystals obtained from solution and thin films from the melt, confirmed the unit cell proposed by Tabor et al. A further confirmation of this structure was given by Uemura et al.,[10] who performed high-resolution electron microscopy studies of solution grown crystals. More recently, Jurga[11] reported NMR spectroscopy measurements giving different results for unoriented samples with different histories. In particular, measurements on crystalline samples of Ryton PPS V-1 (produced by Phillips Petroleum Co.), extracted with water and tetrahydrofuran, were in agreement with the structural model proposed by Garbarczyk, while the results obtained with samples annealed at 540 K after quenching in a mixture of alcohol and dry ice were in agreement with the structure of Tabor et al.

In this paper we report the results of an X-ray analysis of samples of PPS crystallized from the melt and subjected to different thermal and/or mechanical treatments and the results of a detailed conformational analysis and of packing energy calculations by molecular mechanics methods. The results of the energy calculations have been used to evaluate the agreement between the observed and calculated intensities of the X-ray reflections for different conformations of the polymer chain and crystal structures. The purpose of these studies is to refine the crystal structure proposed by Tabor et al.[7] and to attempt to clarify the question as to whether different treatments of PPS polymer samples affect the crystal structure.

Experimental Section

Sample Treatments. The PPS used was Sigma Aldrich powder (catalog no. 18,235-4). The as-received polymer (sample I) was subjected to the following treatments: (i) compression molding at 300 °C for 30 min in a holder under a pressure of 20 MPa and subsequent quenching in a bath of ice and water (sample II); (ii) annealing of sample II at 150 °C for 30 min in an oven (sample III); (iii) compression molding at 300 °C for 30 min in a holder under a pressure of 20 MPa and subsequent cooling in air (sample IV); (iv) extraction with tetrahydrofuran, melting at 300 °C for 2 h under a pressure of 0.05 MPa, and subsequent cooling in the oven (sample V); (v) extrusion from the melt by a syringe (in this way an amorphous unoriented sample is obtained) followed by stretching and annealing for at least 1 h at increasing temperatures up to 280 °C (crystalline oriented samples). The most oriented sample was obtained with a final elongation of about 400% (sample VI).

DSC Analysis. DSC measurements were performed on all samples with a DSC7 Perkin-Elmer calorimeter at a scanning rate of 10 °C/min. The amorphous samples exhibited one exothermic peak (crystallization) at ∼115 °C. The crystalline samples exhibited one endothermic peak (melting) at ∼281 °C.

X-ray Determinations. X-ray analysis was carried out using Ni-filtered Cu Kα radiation. Powder spectra were collected with a Philips PW3710 automated diffractometer operating in the conventional $\theta/2\theta$ Bragg−Brentano geometry. Fiber diffraction patterns were obtained by using two photographic cylindrical cameras with radii of 28.65 and 57.3 mm, respectively. Because of the thinness of the oriented samples, bundles of four fibers, sufficient to obtain good intensities of the reflections, were put in a Lindemann capillary having a diameter of 0.2 mm.

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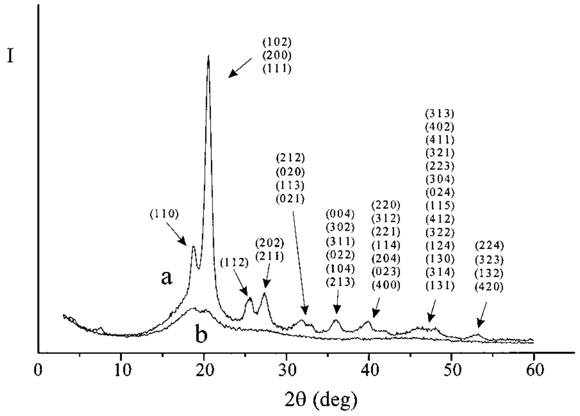

Figure 1. X-ray powder diffraction profiles of sample I (a) and sample II (b) of PPS. The indices of the reflections included in each peak of the crystalline sample are also indicated.

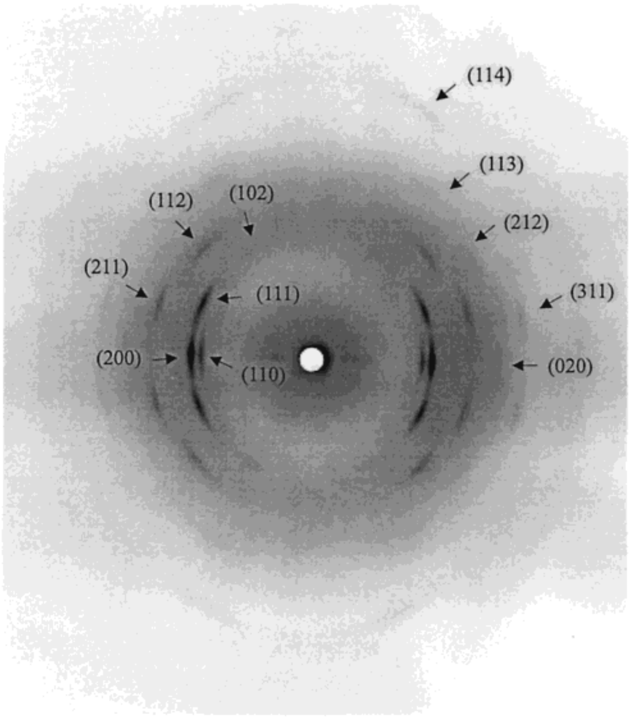

Figure 2. X-ray fiber diffraction pattern of sample VI of PPS obtained by a cylindrical camera. The indices of the most intense reflections are indicated.

Analysis of Diffraction Patterns

Irrespective of thermal and mechanical treatment (samples III−V), the diffraction spectra of crystalline unoriented samples were practically coincident for the positions and for the intensities of all reflections. These spectra are very similar to that of the as-received polymer (sample I). On the contrary, the quenched sample (sample II) exhibited a diffraction profile typical of an amorphous polymer. Figure 1 shows the diffraction patterns of a crystalline sample (sample I) and of the amorphous sample (sample II). The degree of crystallinity determined by the ratio between the crystalline and total (crystalline plus amorphous) areas is 68%.

Figure 2 shows the fiber diffraction pattern of the oriented sample (sample VI). The pattern is very similar both for the positions and for the intensities of the reflections to the fiber diagram of oriented strips reported by Tabor et al.,[7] such that all reflections can be indexed according to the unit cell and the space group proposed in ref 7. Since the 2θ values obtainable from the fiber spectra are in agreement with the maxima of the peaks in the powder spectra, the latter can be also indexed (see Figure 1). This is a clear indication that the crystal structures of both the oriented and the unoriented samples are characterized by the same unit cell and space group.

Molecular Mechanics Calculations

To determine the chain conformation and the mode of packing of the chains, we have calculated the energy of various crystal structures by means of semiempirical potential functions. We have evaluated in two successive steps: (i) the conformational energy of an isolated chain as a function of the internal parameters; (ii) the packing energy of chains in the crystal. To this purpose we have used computer programs developed in our laboratories which can give the results both by maps of the energy as a function of pairs of chosen parameters and by minimizations as a function of all the parameters. These programs have been extensively used for the prediction of crystal structures of polymers in previous papers.[12−21] The lowest energy structures have been considered in the choice of the crystal structure of PPS on the basis of the best agreement with the X-ray data.

Potential Functions. The energy has been calculated as the sum of several contributions, i.e., $E = E_b + E_t + E_{nb}$. The terms E_b and E_t concern only the conformational energy while the term E_{nb} concerns both the conformational and the packing energy. In fact, E_{nb} is the energy contribution due to the interactions between atoms of the same chain separated by more than two bonds or between atoms belonging to different chains.

$E_b = (K_b/2)(\tau - \tau_0)^2$ represents the energy contribution due to the deformation of the bond angle τ with respect to the equilibrium angle τ_0, and K_b is the corresponding energy constant. Only the deformations of the C−S−C angles have been considered, all the other bond angles being fixed at 120°. We have used the value 0.125 kJ $\text{mol}^{-1}\ \text{deg}^{-2}$ and 107.5° for K_b and τ_0, respectively. The value of K_b has been obtained by Musso[22] from vibrational spectra measurements on PPS oligomers.[23] The value of τ_0 was chosen by the procedure described in the following section.

$E_t = (K_t/2)(1 - \cos 2\sigma)$ represents the contribution of the intrinsic torsional potential due to the rotations around single bonds, where σ is the torsion angle and K_t the barrier height. The sign (−) and the 2-fold function are due to the delocalization of π electrons of the sulfur atoms and of the phenylene rings. The value of K_t is 3.2 kJ/mol.[24]

$E_{nb} = Ar^{-12} - Br^{-6}$ is the energy contribution due to the interactions between atoms at a distance r with A and B the repulsive and the attractive constant, respectively. Cutoff distances equal to twice the van der Waals distances (r_0) for the considered atomic species have been adopted. The values of B have been determined by applying the Slater−Kirkwood equation[25] in the slightly modified form reported by Momany et al.[26] and using the polarizabilities and the effective number of electrons reported in the latter paper. The values of A are given by $^1/_2 B r_0^{-6}$. We have adopted values of r_0 that increased with respect to those reported in ref 26 in order to reproduce the specific volume of the unit cell of the crystalline polymer at room temperature. In fact, as pointed out in previous papers,[13−16,20] optimization

Table 1. Values of the van der Waals Distances (r_0) and of the *A* and *B* Parameters of the Nonbonded Energy Term

interacting pair	r_0 (Å)	$A \times 10^{-4}$ (kJ Å^{12} mol^{-1})	B (kJ Å^{6} mol^{-1})
S, S	4.00	118	577
S, C	3.85	159	979
S, H	3.30	16.8	260
C, C	3.70	296	2305
C, H	3.15	32.3	663
H, H	2.60	3.0	195

$l_{S\text{-}C}$ = 1.74 Å
$l_{C\text{-}C}$ = 1.39 Å
$l_{C\text{-}H}$ = 1.08 Å

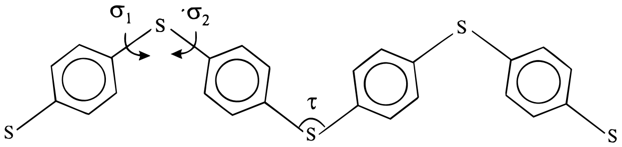

Figure 3. Portion of the chain of PPS considered in the conformational energy calculations with the indication of the variable parameters and of the bond lengths used.

of the packing energy with respect to all the variables, including the cell axes, leads to values of the latter near those that can be extrapolated at 0 K from experiments. It is so because the potential functions do not take into account the thermal vibrations of the atoms. As the temperature increases, the amplitude of the thermal vibrations also increases, and the atoms tend to stay at higher distances, as if the van der Waals radii become greater. The values of the adopted van der Waals distances are shown in Table 1 together with the calculated values of *A* and *B*.

Conformational Analysis. We have performed the conformational analysis on a single polymer chain having all the sulfur atoms in the same plane in a *zigzag* manner, and we have assumed that the experimental *c*-axis comprises two monomeric units (mu), as can be deduced by the fiber spectra. Under these conditions an inversion center lies on each phenylene ring, such that every other ring is correlated by symmetry. The simplest line repetition group[27] that can describe this chain conformation is **t***i*. In this line repetition group no symmetry element correlates consecutive phenylene rings. Line repetition groups (**t***ci* and **t***im*) having higher symmetries arise when the adjacent phenylene rings are also correlated by symmetry elements.

The conformational energy (E_{conf}) has been calculated by taking into account a portion of the polymer chain comprising four mu, as shown in Figure 3. In the same figure the variable parameters and the bond lengths used in our calculations are also indicated. Because of the presence of inversion centers on the phenylene rings, all the bond angles τ assume the same value. As far as the torsion angles are concerned, two independent torsion angles, σ_1 and σ_2, are defined for **t***i* symmetry. The higher symmetries imply a relationship between σ_1 and σ_2, such that in these cases only one torsion angle (named σ) is independent.

The energy has been referred to one monomeric unit. Therefore, we have taken into account the bending term for the deformation of one C−S−C angle and the torsional contributions for the rotations around two adjacent C−S bonds. The nonbonded term has been calculated by taking into account interactions between the atoms of one monomeric unit and all atoms of the macromolecule.

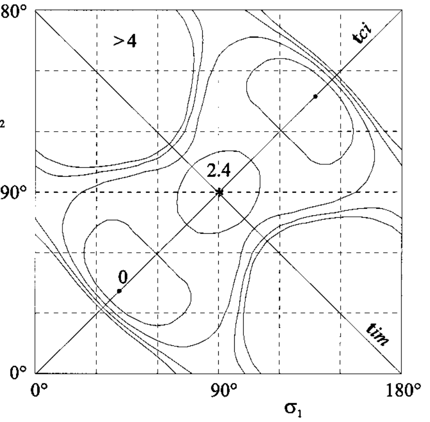

Figure 4. Map of the conformational energy of PPS as a function of σ_1 and σ_2 for the **t***i* line repetition group and for τ = 110°. The level curves are reported at intervals of 1 kJ (mol of mu)$^{-1}$ with respect to the absolute minimum of the map assumed as zero. The asterisk indicates a relative maximum. The diagonal lines represent the loci of the points corresponding to the **t***ci* and to the **t***im* symmetries.

To find the low-energy regions, we have calculated the map of the conformational energy as a function of σ_1 and σ_2. Due to the planarity of the phenylene rings the values of σ_1 and σ_2 are in the range 0°−180°. Figure 4 shows the map calculated for $\tau = 110°$. The map shows two equivalent absolute minima for $\sigma_1 = \sigma_2 \approx 45°$ and for $\sigma_1 = \sigma_2 \approx 135°$, and two equivalent relatively flat regions around ($\sigma_1 = 0°$, $\sigma_2 = 90°$) and ($\sigma_1 = 90°$, $\sigma_2 = 0°$), $\approx$2 kJ (mol of mu)$^{-1}$ higher in energy with respect to the absolute minima.

The conformations corresponding to the line repetition groups having higher symmetry are included in this map. In fact, the diagonal line for which $\sigma_1 = \sigma_2$ represents the loci of the points corresponding to the **t***ci* symmetry characterized by 2-fold axes perpendicular to the chain axis and crossing the sulfur atoms; in this way, adjacent phenylene rings are related by a glide plane parallel to the chain axis. It is worthwhile to note that for σ in the range 35°−75° the energy values lie in a range within 2 kJ (mol of mu)$^{-1}$. Therefore, it is foreseeable that packing interactions, which will be considered below, can play a significant role in determining the positions of the phenylene rings, that is, the value of σ. In this framework, we underline that the intermolecular packing effect which alters the chain conformations from those calculated for single chains was already observed in aromatic polymers[28] as well as in poly(*cis*-1,4-butadiene).[13]

The diagonal line for which $\sigma_1 = 180° - \sigma_2$ ($= -\sigma_2$) represents the loci of the points corresponding to the **t***im* symmetry characterized by mirror planes perpendicular to the chain axis and crossing the sulfur atoms. The corresponding conformations are mostly of high energy.

A map of the conformational energy of a short PPS segment was reported by Jones et al.[29] in a paper concerning the local structure of the polymer in the noncrystalline state. This map is very similar to that of Figure 4 though the latter has been calculated by taking into account a longer chain segment having the **t***i* symmetry and by using increased values of the van der Waals distances for the atomic species.

Minimizations of the conformational energy have been carried out by varying simultaneously the torsion angles and the bond angle τ. The last parameter is of particular

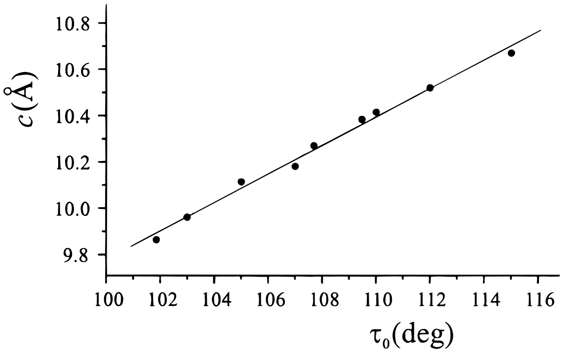

Figure 5. Trend of the chain axis repeat c as a function of τ_0 obtained by the conformational energy minimizations of chains of PPS in the **t***ci* symmetry.

interest because literature data on the C−S−C bond angles are reported in a rather wide range (101°−110°).[7,8,23,30]

A problem in the evaluation of the bending energy arises from the definition of the equilibrium value τ_0 of the C−S−C angle. In this framework we have performed, for chains having the **t***ci* symmetry, a preliminary set of minimizations of the conformational energy as a function of σ and τ for different values of τ_0 in the range 102°−114°. For each minimum energy value we have obtained a value of τ and, as a consequence, have evaluated the chain axis repeat c. Figure 5 shows the trend of c as a function of τ_0. The value of τ_0 corresponding to the experimental value $c = 10.26$ Å is 107.5°, which we have assumed as the equilibrium value for the C−S−C angle in all the following minimizations concerning the different line repetition groups.

We have performed minimizations of the conformational energy for chains having the three different symmetries starting from different significant points of the energy map. All the minimizations have been done both without any constraint on the value of the chain axis repeat and under the constraint of the experimental value $c = 10.26$ Å. For the **t***i* symmetry we have chosen as starting points the minimum-energy point and various points comprised in the wide region around it. Even starting from values of σ_1 and σ_2 very different from each other, the resulting energy minimum shows very similar values of σ_1 and σ_2. In other words, the **t***i* symmetry practically degenerates into the **t***ci* symmetry. The minimizations for the **t***ci* and for the **t***im* line repetition group have been done in order to evaluate the energy costs necessary to obtain chains having these symmetries.

The results of all minimizations are shown in Table 2. The results confirm that the constraint of the perfect **t***ci* symmetry has no energy cost with respect to the constraint of the **t***i* symmetry in the minimized conformations. On the contrary, higher values of the energy are required to realize the **t***im* symmetry.

The values of the energy and of the c axis obtained by using the conformational parameters suggested in ref 8 for the structure of untreated samples are also reported in Table 2. The energy value is very high, so those conformational parameters are unlike for PPS in the crystal state.

Packing Analysis. We have calculated the packing energy (E_{pack}) by considering the nonbonded interactions between the atoms of one monomeric unit of a chosen chain and the atoms of the six neighboring chains according to the symmetry elements of the space group considered. The outer chains have not been considered because the distances between their atoms and the atoms of the chosen chain are higher than cutoff distances. Even if the chain conformation has been taken fixed in each calculation of the packing energy, we have carried out various calculations with chains having various conformations.

Table 2. Values of the Conformational Parameters, of the Energy, and of the Chain Axis Obtained by Minimizations of the Conformational Energy for the Different Symmetries. For Comparison, the Values of the Energy and of the Chain Axis Obtained Using the Conformational Parameters Suggested for the Structure of Untreated PPS in Ref 8 Are Also Reported; the Energy Values Are Referred to the Absolute Value of the Map of Figure 4

symmetry	σ_1/deg	σ_2/deg	τ/deg	E/kJ (mol of mu)$^{-1}$	c/Å
t*i*	46.1	46.9	108.6	−0.2	10.17
t*i*[a]	43.6	43.9	109.9	0.0	10.26
t*ci*	45.9	*b*	108.7	−0.2	10.17
t*ci*[a]	43.6	*b*	110.1	0.0	10.26
t*im*	77.4	*b*	107.0	1.4	10.07
t*im*[a]	74.2	*b*	110.0	1.9	10.26
t*i*	4.2[c]	62.2[c]	105.4[c]	14.9	9.96

[a] Under the constraint of $c = 10.26$ Å. [b] For this symmetry, only one torsion angle is independent (see text). [c] Conformational parameters suggested in ref 8.

We have taken into account chain conformations having **t***ci* symmetry and $c = 10.26$ Å, which corresponds to the bond angle $\tau = 110.1°$, but different orientations of the phenylene rings, that is, different values of σ. The values of σ are chosen in the wide range in which the conformational energy is low. We have used the unit cell parameters and the space group proposed by Tabor et al.[7] and confirmed by our analysis of diffraction patterns. Assuming as crystallographic elements the symmetry elements of the chains, i.e., the inversion centers, the glide plane, and the 2-fold axes, the positions of the chains in the *Pbcn* space group are fixed, as shown in Figure 6. Hence, in the calculations of the packing energy in this space group the only variable is the conformational parameter σ.

Figure 7 shows the trends of the conformational energy, of the packing energy, and of the total (conformational plus packing) energy as a function of σ. The minimum of the curve of the packing energy is sharper than the minimum of the conformational energy, and it corresponds to $\sigma = 35°$, significantly lower with respect to the σ value of the minimum of the conformational energy ($\sigma = 43.6°$, see also Table 2). As a consequence, the minimum of the total energy is rather sharp and centered at $\sigma = 39°$ with energy increases of about 2 kJ (mol of mu)$^{-1}$ in a range of ±5° around it. These results indicate that, even if the phenylene rings can be expected to be almost free rotating in a wide range of σ in the isolated chain, the packing forces limit remarkably these conformational degrees of freedom.

Calculations of the Discrepancy Factor *R*

The models of the chain conformation and of the mode of packing of PPS obtained by molecular mechanics can be used for calculating the diffracted intensities of the reflections; these can be then compared with the data obtained by X-ray spectra. We report here the comparison between calculated and observed intensities for a powder spectrum. We have calculated the X-ray diffraction intensities for the structures corresponding to σ

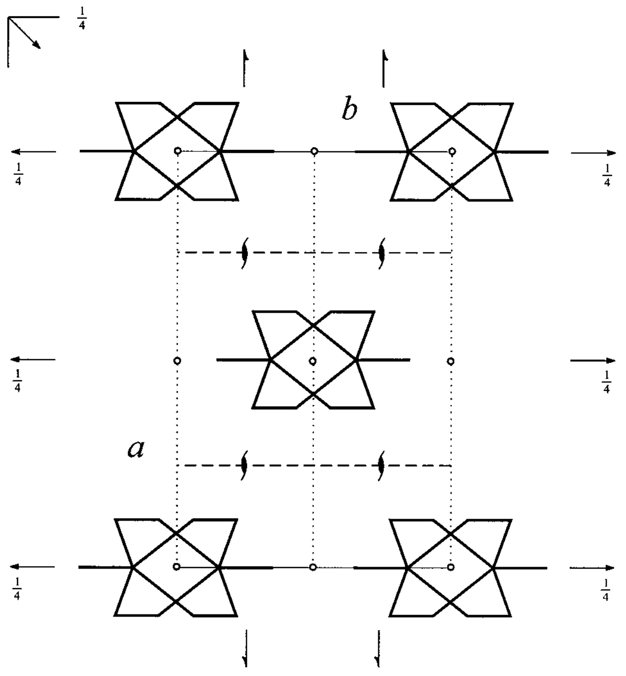

Figure 6. Projection in the *ab* plane of the content of the unit cell of PPS in the *Pbcn* space group with the indication of the symmetry elements. The symbols of the symmetry elements are in agreement with ref 31.

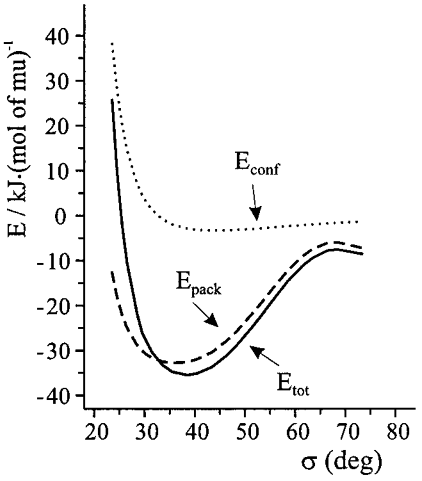

Figure 7. Trends of the conformational energy (E_{conf}), of the packing energy (E_{pack}), and of the total energy (E_{tot}) of PPS as a function of σ.

values in a range of ±15° centered around the σ value (39°) of the minimum-energy point. The calculated X-ray diffraction intensities have been obtained by the following formula: $I_c = |F_c|^2 M\mathrm{LP}$, where F_c is the structure factor obtained using the atomic factors from ref 32 and a thermal factor $B = 8$ Å^2, M is the multiplicity factor, and $\mathrm{LP} = (1 + \cos^2 2\theta)/(2 \sin^2 \theta \cos \theta)$ is the Lorentz-polarization factor for the X-ray powder diffraction. A quantitative comparison between calculated and experimental intensities has been performed by evaluating the experimental intensities from the X-ray powder diffraction pattern reported in Figure 1. The experimental intensities I_o have been obtained by measuring the areas of the peaks in the X-ray powder pattern after the subtraction of the amorphous area. The discrepancy factor R has been evaluated as $R = (\Sigma|I_o - I_c|/\Sigma I_o) \times 100$, where I_c represents the summation over all reflections included in the 2θ range of the corresponding observed reflection peak, as reported in Figure 1. The summation is taken over all the calculated reflections in the range from 5° to 60° of 2θ.

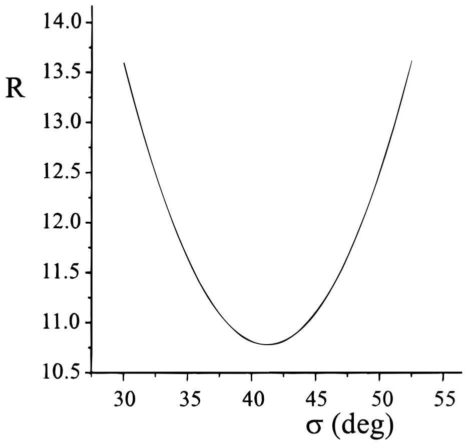

Figure 8. Trend of the discrepancy factor R as a function of σ for PPS.

Table 3. Values of the Conformational Parameter σ, of the Discrepancy Factor R, and of the Energy E for the Indicated Structures

structure	σ/deg	R	E/kJ (mol of mu)$^{-1}$
minimum energy	39	10.9	−34.9
minimum R	41	10.8	−34.5
structure of ref 7	45	11.1	−32.3

Figure 8 shows the trend of the discrepancy factor R as a function of σ. The lowest value of R is10.8 and is obtained for $\sigma = 41°$, very close to the value (39°) corresponding to the minimum-energy point. The value of R obtained for $\sigma = 45°$, proposed by Tabor et al.,[7] is slightly higher ($R = 11.1$).

The most significant results of the energy and of the discrepancy factor calculations are summarized in Table 3. We underline that the minimum-energy structure and the minimum-R structure are very similar, the differences of the values of σ, R, and energy being equal to 2°, 0.1, and 0.4 kJ (mol of mu)$^{-1}$, respectively. On the contrary, the calculated energy for the structure proposed by Tabor et al. is 2.6 kJ (mol of mu)$^{-1}$ higher with respect to the absolute energy minimum.

Conclusions

Oriented samples and powder of PPS crystallized from the melt under different thermal and/or mechanical treatments are found to always give the same crystal structure, which is in substantial agreement with the structure proposed by Tabor et al.[7]

A detailed conformational analysis carried out on isolated chains having two monomeric units in the *c*-axis has indicated that in the crystalline field the torsion angles around the bonds adjacent to the sulfur atom assume the same value; i.e., the best chain symmetry is **t***ci*. However, the conformational analysis has also indicated a high degree of freedom in the isolated chains for the rotation of the phenylene rings around the S−S segments. Conversely, the packing energy calculations have clearly indicated that the rotational freedom is very restricted in the crystal. The best value of σ obtained by both intra- and intermolecular energy calculations is 39°, and the energy increase is no higher than 2 kJ (mol of mu)$^{-1}$ in a range of ±5° around it.

The results of the energy calculations are in very good agreement with the structure that we have obtained comparing the calculated and the observed intensities for the X-ray powder spectrum.

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