Crystal structure of poly(*p*-phenylene sulfide) by nuclear magnetic resonance spectroscopy

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Calculations of intramolecular and intermolecular interactions, giving the contributions to the nuclear magnetic resonance second moment for poly(*p*-phenylene sulfide) (PPS), have been carried out. Second-moment values of the PPS rigid lattice before and after heat treatment have been measured. Good agreement between theoretical and experimental data has been obtained. The parameters of the unit cell for the PPS 'asymmetric model' have been determined.

INTRODUCTION

The crystal structure of poly(*p*-phenylene sulfide) (PPS)
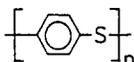
subjected to heat and mechanical treatment was determined by Tabor et al.[1] and confirmed by Lovinger et al.[2]. According to these structures, the chains pass through the corners and centre of the orthorhombic unit cell. The sulfur atoms are in the (1 0 0) plane and are arranged in a 'zig-zag' form. The planes of the phenylene rings are at angles of $+45°$ and $-45°$ with respect to the (1 0 0) plane. The covalent angle at the sulfur atoms is $110°$. The unit cell of this system has the following lattice parameters: $a = 8.67$ Å, $b = 5.61$ Å and $c = 10.26$ Å.

The crystal structure of PPS was also examined by Garbarczyk et al.[3-6] using as a model low-molecular-weight phenylene sulfide compounds. The phenylene rings in this low-molecular-weight structure are oriented asymmetrically with respect to the crystallographic (1 0 0) plane. Garbarczyk does not give details of the PPS crystal structure, but suggests that the PPS may have different structure than that of Tabor et al.[1]

The PPS crystal structure was also investigated by means of n.m.r. spectroscopy by Jurga et al.[7] and Schlick et al.[8]. The calculated n.m.r. second moments for protons, using the structural data of Tabor et al.[1], differ from the experimentally obtained values.

The aim of this study is to explain the discrepancy between the observed and calculated second moments, using the available X-ray structural data of PPS[1] and the data on low-molecular-weight oligomers of phenylene sulfides obtained by Garbarczyk[3-6]. By taking these structural data we consider two crystal models of PPS. The first model is characterized by the symmetric position of the phenylene rings with respect to the (1 0 0) crystallographic plane ('symmetric model'), while the second one is characterized by the asymmetric position

of these rings with respect to the (1 0 0) crystallographic plane ('asymmetric model'). The results of the calculated n.m.r. second moments for these models are compared with the experimental data for virgin and thermally treated PPS.

EXPERIMENTAL

Poly(*p*-phenylene sulfide), type Ryton PPS V-1 produced by Phillips Petroleum Co., was the principal material (virgin) used in the n.m.r. spectroscopic studies. Three different modifications of PPS, denoted here as samples I, II and III, are considered.

Sample I obtained from powdered polymer initially extracted with water and tetrahydrofuran using 170 cycles in a Soxhlet column was then dried for 140 h at 293 K and 10^{-5} Torr vacuum. An elemental analysis showed that after the extraction the polymer's purity was 99.19% and its empirical formula $C_6H_{3.96}S_{0.95}$ (ref. 9). The polymer's average molecular weight, determined by end-group analysis of the chloride content, was estimated to be 10 800.

Sample II was made from sample I by melting it at about 580 K under a pressure of 0.03 MPa in a vacuum of about 10^{-5} Torr and next rapid cooling in a mixture of alcohol and dry ice[10]. The degree of crystallinity of the obtained film, determined by X-ray diffraction, was 31%[11].

Sample III was obtained by additional heat treatment of sample II for 2 h in vacuum at 540 K.

The rate of heating or cooling for all samples was about 10 K h^{-1}.

For n.m.r. studies the PPS samples were placed in glass ampoules under vacuum. Measurements of linewidths with a continuous-wave spectrometer at a frequency of 30 MHz[12] for samples I and II were made from 295 to 120 K and then back to 540 K, while for sample III from 540 K to 120 K.

The experimental values of the linewidth as a function
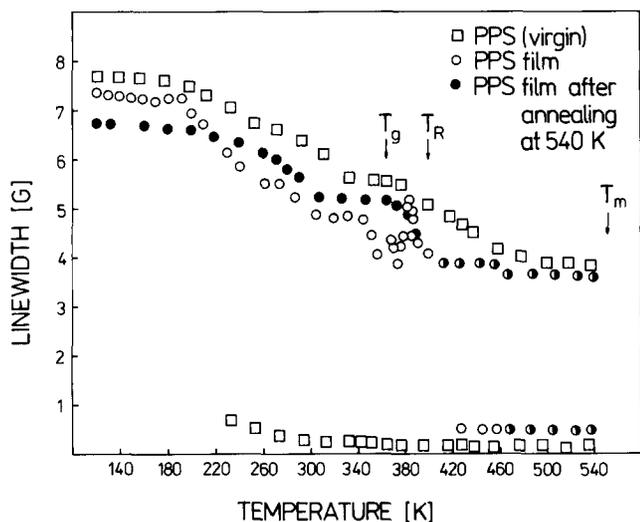
Figure 1 N.m.r. linewidth for virgin PPS (sample I) and PPS films (samples II and III)

of temperature for all studied samples are presented in *Figure 1*.

The temperature dependence of the linewidth for sample I is the same as that measured earlier[9] and does not show any specific behaviour.

For sample II on lowering the temperature from 295 K to 120 K an increase of the linewidth to the value of 7.4 G at 120 K is observed. The change of the linewidth in this temperature range is the same for both cooling and heating the sample. At 295 K the linewidth amounts to 4.8 G and remains the same up to 345 K. A further increase of temperature causes a decrease of the linewidth to the value of 3.8 G at 365 K, which is then followed by a sharp increase of the linewidth to the value of 5.2 G at 385 K. Above this temperature the linewidth decreases again, reaching the value of 3.5 G at 540 K.

If an annealing process of sample II is taking place in the temperature range from 400 to 540 K, then a quite different temperature dependence of the linewidth from 385 to 120 K, as compared to that of the unannealed sample II, is observed. The linewidth at 120 K of the annealed sample III is smaller than that for unannealed sample II.

We observe also that, during the heating process above 385 K, sample II changes colour from a transparent light beige to non-transparent, indicating thus that crystallization occurs.

Experimental second moments were determined only for samples I and III by the graphic integration of the surface of the broad line spectrum. The amorphous phase contribution to the second moment of the sample III at 130 K is negligible (see *Figure 2b*).

The observed values of the rigid lattice second moments at 120 K are $6.9 \pm 0.5 \, G^2$ for sample I and $5.6 \pm 0.5 \, G^2$ for sample III.

THEORETICAL

According to n.m.r. spectroscopic investigations, the solid-state structure is rigid if the frequency of molecular motions is lower than the resonance linewidth. This is the case below the glass transition temperature, T_g, of PPS. The reorientations of phenylene groups are totally hindered even below 200 K[7,8].

The second moment for a rigid lattice of single crystals can be estimated as[13]:

$$M_2 = \frac{3}{4} \frac{I(I+1)}{N} \gamma^4 \hbar^2 \sum_{i \neq j} (3 \cos^2 \theta_{ij} - 1)^2 r_{ij}^{-6} \qquad (1)$$

where I = the nuclear spin value, N = the number of nuclear sites at which summation is done, γ = the gyromagnetic ratio, $\hbar$ = Planck constant divided by 2π, and θ_{ij} = the angle between internuclear vector r_{ij} and the direction of the magnetic field.

For random orientations of the crystallites in polymers, after averaging of the angular relationship $(3 \cos^2 \theta_{ij} - 1)$ over all possible directions, equation (1) can be written as:

$$M_2 = \frac{3}{5} \frac{I(I+1)}{N} \gamma^4 \hbar^2 \sum_{i \neq j} r_{ij}^{-6} \qquad (2)$$
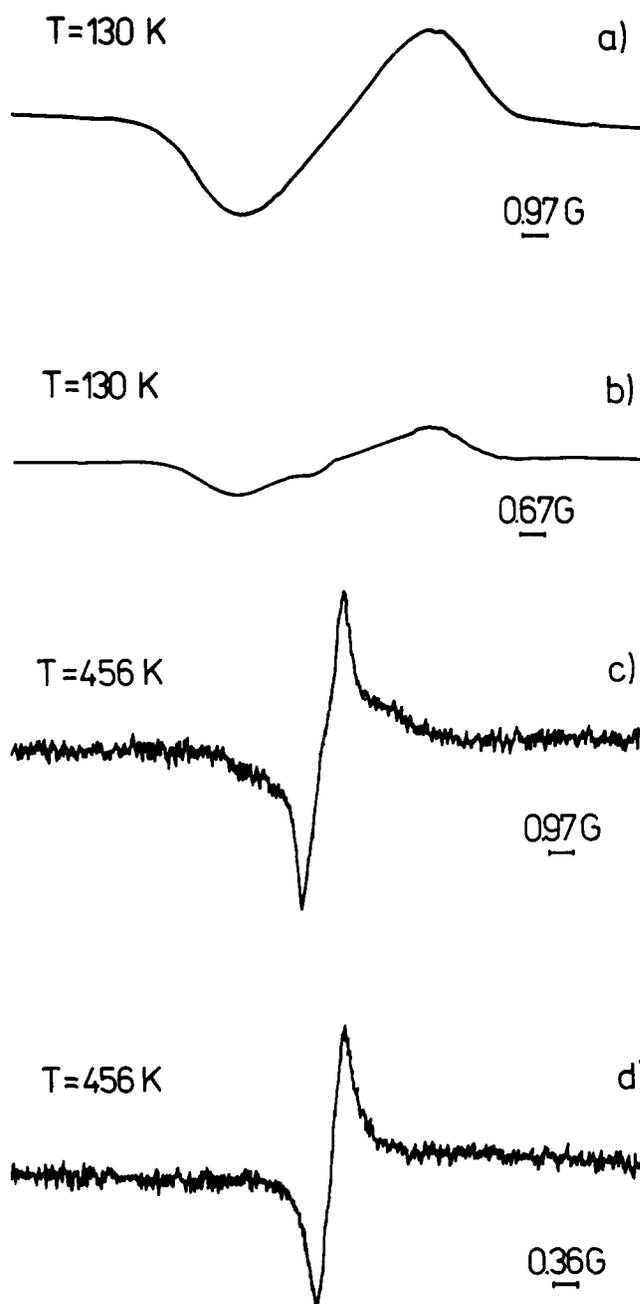
Figure 2 Spectrum of PPS film (sample III) for the broad lines (a, c) and for narrow lines (b, d) after heat treatment at different temperatures

Equation (2) was used to calculate both the intramolecular part (M_2^{intra}) and the intermolecular part (M_2^{inter}) of the second moment. In the case of poly(*p*-phenylene sulfide), M_2^{intra} describes all interactions between the protons within the polymer chain, while M_2^{inter} describes the interactions between protons of all adjacent chains contained within a sphere of suitable large radius. The sum of these two parts, calculated on the basis of structural data of PPS, can be compared with the second moment determined experimentally.

ANALYSIS OF PPS CRYSTAL STRUCTURE

The 'symmetric model' of the PPS structure

The planes of the phenylene rings in the crystal structure of PPS given by Tabor *et al.*[1] are arranged symmetrically with respect to the (1 0 0) plane. Calculation of dipolar proton interactions for this arrangement of PPS ('symmetric model') was carried out for 28 polymer chains passing through the *X*, *Y* plane (*Figure 3*). The intramolecular and intermolecular parts of the n.m.r. second moment were obtained for all protons within a sphere of radius 12 Å. For distances greater than this, the contributions to the second moment are negligibly small. The starting point for the calculations took into account the coordinates of the atoms situated in the (1 0 0) crystallographic plane, i.e. in the plane of the sulfur atoms.

The minimum total dipolar interaction (the greatest distances) between all protons in the space considered was obtained by rotating the chains passing through the centres of the 14 elementary cells about the *Z* axis.

The intramolecular contribution to the second moment was estimated to be 2.1 G^2. It was found that the intermolecular contribution calculated as a function of

Figure 4 Second moment as a function of chain orientation for the PPS 'symmetric model'

the rotation angle reached its minimum value of 1.4 G^2 at an angle of 0°. Therefore the total minimum second moment for the PPS 'symmetric model' is:

$$M_2^{min} = M_2^{intra} + M_2^{inter} = 3.5 \text{ G}^2$$

This result is in agreement with that obtained by Schlick *et al.*[8]. The second moment depends on the rotation angle chosen for the polymer chains, as seen in *Figure 4*. The minimum value of the second moment differs significantly from the experimental result of sample III and also from sample I.

The large difference between the observed and calculated values of second moment suggests that the PPS sample is a more packed crystal structure than would arise from the crystal structure of Tabor *et al.*[1].

In order to explain this, we discuss in the following section a crystal structure derived from the crystallographic data of Garbarczyk[3-6].

The 'asymmetric model' of the PPS structure

According to Garbarczyk[5] calculations of intramolecular and intermolecular interactions for two phenylene sulfide trimers, the arrangement of phenylene rings in this compound is asymmetric with respect to the crystallographic (1 0 0) plane. The planes of these rings form angles of 4.15° and 59.62° with this crystallographic plane. The interaction energy between two phenylene trimers is a minimum when one of the trimers passing through one of the unit-cell corners is shifted along the *X*, *Y* and *Z* axes by −0.37 Å, −0.17 Å and +1.6 Å,

Figure 3 The PPS unit cell for 'symmetric model' (thin lines) and for 'asymmetric model' (thick lines)

respectively, with respect to the original system of coordinates. In addition this trimer is rotated about the Z axis through an angle of $+10°$ out of the (1 0 0) plane. The other trimer passing through the cell centre remains in the (1 0 0) plane. The covalent angle at the sulfur atoms is then $106.63°$.

The crystal structure model of PPS, which consists of asymmetric phenylene sulfide trimers and repeats in space, thus forming chains, was taken in our paper as the basis for the second-moment calculations ('asymmetric model'). The intramolecular and intermolecular parts of the second moment were obtained for all protons within a sphere of radius 12 Å. For distances greater than this, the contributions to the second moment are negligibly small. In this model 28 polymer chains passing through the X, Y plane were taken into account. The starting point for the calculations took into account the coordinates of the atoms situated in the (1 0 0) crystallographic plane, i.e. in the plane of the sulfur atoms.

The intramolecular part of the second moment was calculated for the interactions between the 24 protons from the six rings in the chain. $M_2^{intra} = 4.4\,G^2$ was obtained for the 'asymmetric model'.

The calculation of M_2^{inter} for this model required the spatial coordinates of all the protons in the 28 polymer chains mentioned above. These coordinates, with respect to the corners and the centre of the unit cell, can be determined using the following relations:

1. $0.5 - x, 0.5 + y, z$

2. $x, y + 1, z$

3. $x + 1 - k, y + 1 - l, z + m$

4. $x + 1, y, z$

5. $x + k, y + 1, z - m$

where the indices 1 to 5 indicate the particular chain in the unit cell, as shown schematically in *Figure 3*. The coefficients k, l, m are the ratios of the spatial shift values a_1, b_1, c_1 respectively of the phenylene sulfide trimers to the lattice parameters a, b and c' with respect to the origin of the coordinate system. These values are also given in *Figure 3*. The lattice parameter c' in this case is 10.09 Å (ref. 6). Knowledge of the coefficients k, l, m allows us to determine the coordinates of the protons of the remaining 23 chains.

The minimum total dipolar interaction between all protons in the space considered (radius 12 Å) was obtained by rotating the chains passing through the centres of the 14 elementary cells about the Z axis.

M_2^{inter} was calculated as a function of the rotation angle of the chains for the 'asymmetric model' and a minimum value of $M_2^{inter} = 2.2\,G^2$ for the angle of $+10°$ was obtained. The total value of the second moment is then:

$$M_2^{min} = M_2^{intra} + M_2^{inter} = 6.6\,G^2$$

The second moment calculated as a function of rotation angle is shown in *Figure 5*.

It must be pointed out that any other orientation of the chains passing through the corners and the centre of the cell for which the second moment is a minimum always gives the angle of 10° between the planes that include these chains.

DISCUSSION

The distance between protons in equation (1) determines the value of the second moment, which is different for each of the models considered. Since very good agreement between the second moment calculated for the 'asymmetric model' and the experimental result for sample I not subjected to heat treatment is obtained, we believe that this model gives a correct description of the structure. Comparison of the calculated intermolecular parts of the second moment for both structural models indicates that the 'asymmetric model' exhibits a more compact structure. This is in agreement with the suggestion made by Garbarczyk[5] for phenylene sulfide trimers.

The dependence of the second moment as a function of the chain rotation angle about the Z axis, presented in *Figure 5*, shows the asymmetric character of the potential barrier for such a motion. This barrier is very high for rotation angles smaller than $+10°$, but is lower for larger rotation angles, and tends to create a second minimum near $+38°$. There is a further increase in the second moment at angles greater than $+38°$. The probability that the chains will be oriented in this metastable position seems to be very small, although one cannot eliminate such a possibility. It seems quite probable that the chains passing through the unit-cell centres are rotated by $+10°$ with respect to the (1 0 0) crystallographic plane. This agrees with the results presented by Garbarczyk[5]. The unit cell of that model can be characterized by the lattice parameters: $a = 8.67$ Å, $b = 5.61$ Å, $c' = 10.09$ Å, $\alpha = 79.36°$, $\beta = 73.43°$
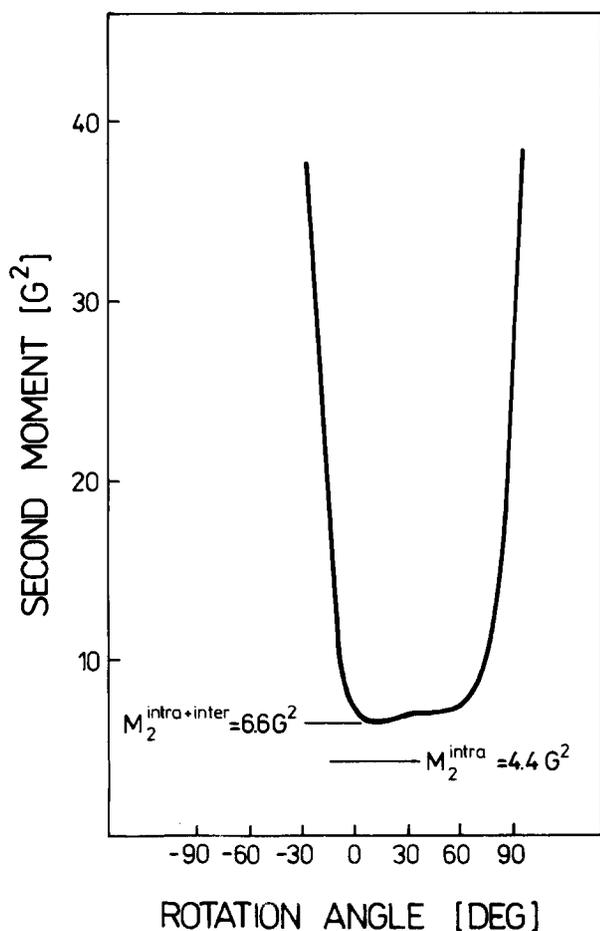
Figure 5 Second moment as a function of chain orientation for the PPS 'asymmetric model'

and $\gamma = 93.20°$, which correspond to a triclinic crystallographic system.

The heat treatment process carried out at temperatures higher than the PPS recrystallization temperature, T_r, of 400 K may lead to a new crystal structure, a considerable part of which can be described by the 'symmetric model'. The transition from one to another structure is supposed to be connected with the polymorphic transformation, which can be considered as a diffusional phase transition of the first order[14]. During the heat treatment of PPS, a change in the unit-cell parameters takes place. As a result of this transformation, the coefficients k, l, m of the atom coordinates in the 'asymmetric model' are equal to zero and the value of the lattice parameter c' increases to $c = 10.26$ Å, i.e. to the value given by Tabor *et al.*[1].

The observed 1 G sharp increase of the linewidth near the temperature of 385 K is not due to a motional process but rather is believed to be caused by structural changes. A similar increase of the linewidth was also observed in the PPS R-6 sample[7], obtained during an industrial heat treatment processing[15] for which d.t.a. studies[7,16] show the existence of a very strong exothermic effect in the same temperature range as for our sample II. This behaviour is connected with the recrystallization temperature of PPS.

The difference between second-moment values calculated for the 'symmetric model' and observed for the thermally treated polymer can arise from the fact that the transition from the 'asymmetric' structure to the 'symmetric' one is not complete, implying that after heat treatment there is a part of the primary structure not subjected to the transformation. This could be the reason for the experimental second-moment value of the thermally treated polymer being always greater than the calculated value.

Thus the reported early inconsistency between the calculated and the experimental second-moment values[7,8] arises from the fact that the PPS structural data[1],

obtained after heat treatment, were used for the calculations of the second moment. On the other hand, the measurements of second moments were carried out on PPS samples that were not thermally treated.

ACKNOWLEDGEMENTS

REFERENCES

1   Tabor, B. J., Magre, E. P. and Boon, J. *Eur. Polym. J.* 1971, 7, 1127
2   Lovinger, A. J., Padden, F. J. Jr and Davis, D. D. *Polymer* 1988, 29, 229
3   Andretti, G. D., Garbarczyk, J. and Królikowska, M. *Crystal Struct. Commun.* 1981, 10, 789
4   Garbarczyk, J. *Makromol. Chem.* 1986, 187, 2489
5   Garbarczyk, J. *Polym. Commun.* 1986, 27, 335
6   Garbarczyk, J. (unpublished data)
7   Jurga, J., Eckert, H. and Müller-Warmuth, W. *Z. Naturforsch.* 1979, 34a, 1216
8   Schlick, S. and McGarvey, B. R. *Polym. Commun.* 1984, 25, 369
9   Hruszka, P., Jurga, J. and Brycki, B. *Polymer* 1992, 33, 248
10 Jurga, J., Hruszka, P. and Gruszka, W. Polish Patent P-282955, 1989
11 Hruszka, P., Garbarczyk, J. and Jurga, J. in preparation; Hruszka, P. *PhD Thesis* Technical University of Poznań, 1991 (in Polish)
12 Jurga, J. *Scientific Instrumentation* 1988, 3, 67
13 Van Vleck, J. H. *Phys. Rev.* 1948, 74, 1168; *Phys. Rev.* 1962, 37, 647
14 Tobolsky, A. V. and Canter, N. M. 'Transitions and Relaxations in Polymers' (Ed. R. F. Boyer), Am. Chem. Soc. Symp., New Jersey, 1965, *J. Polym. Sci. (C)* 1965, 14, 30–7
15 'Ryton[R] Polyphenylene Sulphide Resins', New Product Information, Phillips Petroleum Co., 1969
16 Brady, D. G. *J. Appl. Polym. Sci.* 1976, 20, 2541